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PREFACE

THE publication of this, the sixteenth volume, marks the completion of the *Comprehensive Treatise on Inorganic Chemistry* as planned. It has been a heavy task to prepare a comprehensive review of so vast a field, and it has inevitably taken a considerable time to complete. The first volume was published in 1922, and succeeding volumes have appeared at regular intervals, until with the publication of the present volume the ordered treatment of the subject has reached its appointed goal. Every attempt has been made to ensure that each volume embodies the information available when sent to press and subsequent developments can readily be traced in the Abstracts of the Chemical Societies. There have, however, been great developments in recent years and many important discoveries have been made, particularly in connection with the elements which were treated in the early volumes. These developments have rendered it advisable to prepare two *Supplementary Volumes*, which will bring the subjects up to date and include the results of the most recent research.

There is also an ill-defined borderland between Organic and Inorganic Chemistry, particularly in connection with some of the Carbon Compounds of Hydrogen and Nitrogen. It has therefore been decided to plan and prepare a special volume dealing with these borderland compounds. The publishers are making the necessary arrangements for this work to be done, and it is hoped that these three Supplementary Volumes will still further increase the usefulness of the *Comprehensive Treatise.*

It is a very great pleasure to me to thank Messrs. L. S. Theobald, M.C., A.R.C.S., A. T. Green, F.Inst.P., A.I.C., and F. H. Clews, M.Sc., A.I.C., for their great assistance in reading the proofs of the whole series of volumes and for the many valuable suggestions which they put forward. I would also thank the typists, and those who have checked the references.

CONTENTS

CHAPTER LXXIV

PLATINUM

ABBREVIATIONS

aq. = aqueous

atm. = atmospheric or atmosphere(s)

at. vol. = atomic volume(s)

at. wt. = atomic weight(s)

T° or °K = absolute degrees of temperature

b.p. = boiling point(s)

θ° = centigrade degrees of temperature

coeff. = coefficient

conc. = concentrated or concentration

dil. = dilute

eq. = equivalent(s)

f.p. = freezing point(s)

m.p. = melting point(s)

mol(s) $= \left\{\begin{array}{l}\text{gram-molecule(s)}\\ \text{gram-molecular}\end{array}\right.$

mol(s). $= \left\{\begin{array}{l}\text{molecule(s)}\\ \text{molecular}\end{array}\right.$

mol. ht. = molecular heat(s)

mol. vol. = molecular volume(s)

mol. wt. = molecular weight(s)

press. = pressure(s)

sat. = saturated

soln. = solution(s)

sp. gr. = specific gravity (gravities)

sp. ht. = specific heat(s)

sp. vol. = specific volume(s)

temp. = temperature(s)

vap. = vapour

In the **cross references** the first number in clarendon type is the number of the volume; the second number refers to the chapter; and the succeeding number refers to the "§," section. Thus **5.** 38, 24 refers to § 24, chapter 38, volume 5.

The oxides, hydrides, halides, sulphides, sulphates, carbonates, nitrates, and phosphates are considered with the basic elements; the other compounds are taken in connection with the acidic element. The double or complex salts in connection with a given element include those associated with elements previously discussed. The carbides, silicides, titanides, phosphides, arsenides, etc., are considered in connection with carbon, silicon, titanium, etc. The intermetallic compounds of a given element include those associated with elements previously considered.

The use of **triangular diagrams** for representing the properties of three-component systems was suggested by G. G. Stokes (*Proc. Roy. Soc.*, **49**. 174, 1891). The method was immediately taken up in many directions and it has proved of great value. With practice it becomes as useful for representing the properties of ternary mixtures as squared paper is for binary mixtures. The principle of triangular diagrams is based on the fact that in an equilateral triangle the sum of the perpendicular distances of any point from the three sides is a constant. Given any three substances *A*, *B*, and *C*, the composition of any possible combination of these can be represented by a point in or on the triangle. The apices of the

triangle represent the single components *A*, *B*, and *C*, the sides of the triangle represent binary mixtures of *A* and *B*, *B* and *C*, or *C* and *A*; and points within the triangle, ternary mixtures. The compositions of the mixtures can be represented in percentages, or referred to unity, 10, etc. In Fig. 1, pure *A* will be represented by a point at the apex marked *A*. If 100 be the

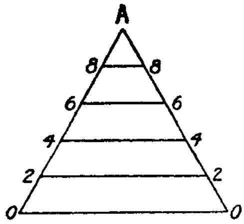

Fig. 1.

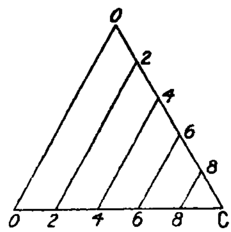

Fig. 2.

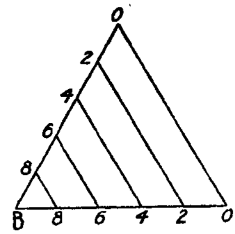

Fig. 3.

standard of reference, the point *A* represents 100 per cent. of *A* and nothing else; mixtures containing 80 per cent. of *A* are represented by a point on the line 88, 60 per cent. of *A* by a point on the line 66, etc. Similarly with *B* and *C*—Figs. 3 and 2 respectively. Combine Figs. 1, 2, and 3 into one diagram by superposition, and Fig 4 results. Any point in this

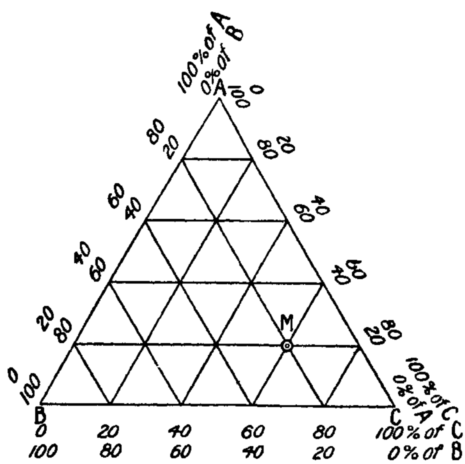

Fig. 4.—Standard Reference. Triangle.

diagram, Fig. 4, thus represents a ternary mixture. For instance, the point *M* represents a mixture containing 20 per cent. of *A*, 20 per cent. of *B*, and 60 per cent. of *C*.

CHAPTER LXXIV

PLATINUM

§ 1. The History of the Platinum Metals

PLATINUM is one member of a family of six elements called the **platinum metals.** They usually occur together so that before the discovery of the companion elements, the term platinum was applied to an alloy with platinum as the dominant metal. The same thing is often done to-day. The platinum metals, with their sp. gr., are as follow:

Platinum metals	Heavy	PLATINUM	(21·45)
		IRIDIUM	(22·38)
		OSMIUM	(22·47)
	Light	PALLADIUM	(11·90)
		RHODIUM	(12·10)
		RUTHENIUM	(12·26)

M. Berthelot[1] reported that an Egyptian casket, found at Thebes, and dating from the seventh century B.C., contained platinum, or rather an alloy of platinum, iridium, and gold. There is, however, no evidence to show that the alloy was to the Egyptians anything more than a metal. In 1790, A. M. Cortenvois tried to prove that the *electrum*—**3**. 23, 1—of the ancients was platinum, and J. S. C. Schweigger, that the electrum mentioned by Pausanis, in his *Περίηγησις*, written about the second century of our era, was also platinum. The following passage from Pliny's *Historiæ naturalis* (**34**. 47), written in the first century of our era, has also been quoted in support of the assumption that *cassiteros*, or *plumbum candidum*, was platinum. Pliny said:

It is now known that it (cassiteros) is a production of Lusitania and Gallæcia. It is a sand found on the surface of the earth, and of a black colour, and can be detected only by its weight. It is mingled with small pebbles, particularly in the dried beds of rivers. The miners wash this sand, and calcine the deposit in a furnace. It is also found in the gold mines that are known as *alutiæ* or *talutiæ*, the stream of water which is passed through them detaches certain black pebbles mottled with small white spots and of the same weight as gold. Hence it is that they remain with gold in the baskets in which it is collected; and being separated in the furnace, are then melted, and become converted into *album plumbum*.

F. Hoefer, and C. de Paravey suggested that the "heavy black pebbles" contained platinum presumably because of their weight, but Pliny's ideas of specific gravity were very vague, and in one place he even said that lead is heavier than gold. H. Kopp, and E. L. Schubarth very rightly considered that these far-fetched allusions have no connection at all with platinum. In the sixteenth century, J. C. Scaliger,[2] writing against G. Cardanus' dictum that all metals are fusible, said that there is a metallic substance in the mines of Mexico and Darian (Panama) which cannot be melted in the Spanish furnaces. It is considered that this metallic substance was probably that which was afterwards called platinum because platinum is now known to occur in these very districts. A. N. von Scherer also said that from a reference in B. A. Balbin's *Epitome* it appears as if platinum was known to the Bohemian Jesuits at the end of the sixteenth century. Towards the middle of the eighteenth century, A. de Ulloa accompanied the expedition sent from France to measure the arc of the meridian at the equator, and in his account

of the voyage, he mentioned that in the mines of El Chocò, Colombia, South America, there is an unworkable, metallic stone called platina which makes even gold ores useless if it is associated with them in large proportions. The South American platinum mines were described by F. J. de Caldas, G. Mollien, T. C. de Mosquera, J. M. Restrepo, V. Restrepo, and A. M. del Rio. E. P. C. Meyer wrote on the history of platinum.

About 1741, W. Brownrigg received a specimen of native platina from C. Wood, a metallurgist in Jamaica, who said that he had obtained it from Carthagina, Granada. The metal was examined by W. Watson, who regarded it as a semi-metal. Other specimens from Spanish America found their way into Europe about this time, and were examined notably by T. Scheffer, A. S. Marggraf, W. Lewis, P. J. Macquer and A. Baumé, P. Bergsöe, etc. Some of the early descriptions were based on the properties of the crude mineral, and did not apply to platinum *per se*.

Some of the early specimens of platina were contaminated with minute globules of mercury because the mineral had been previously ground with mercury in mills with the object of dissolving out the gold. Until assayers had learned to deal with the alloy of platinum and gold in cupellation processes, gold could be adulterated with platina without being detected by the sp. gr. tests, or by cupellation processes then available. W. Lewis reported that some bars of gold had been received from some Spaniards in payment for goods, and that the bars were very brittle, and could not be refined so that they were "quite useless"; and also, on this account, the Dutch refiners at Dort are said to have called platina *diabolus metallorum*. It was also said that the King of Spain had ordered the mines that afford the platina to be closed in order to prevent the fraudulent adulteration of gold; C. L. Berthollet and B. Pelletier said that the Spanish Government, for a similar reason, had ordered a consignment of platinum or gold debased by platinum to be thrown into the sea.

The term *platina* is the diminutive form of the Spanish *plata*, silver, and it was applied in allusion to the silvery colour of the metal. T. Scheffer called it *aurum album* or white gold in allusion to its smaller value, or, as E. Uricoechea suggested, to its silver-white colour, and to its close resemblance to gold in many of its properties. It was also called *the seventh metal*, since, excluding alloys, six elemental metals were then known—**1.** 1, 1. It was also called *platina del Pinto*, since some specimens from South America came from the neighbourhood of the river—Rio di Pinto. It was also called *Juan blanco*, which, according to W. Lewis, arose from some frauds practised with it, from the difficulty in separating from it any associated gold, from its refractoriness in the hands of workmen, just as *black-jack* is applied to a mock ore which outwardly resembles the true metallic ore, but in the usual way of trials does not yield any metal. *Juan blanco* would then be equivalent to *white-jack*, *white rogue*, or *white mock metal*. More probably Juan blanco refers to the San Juan in the El Chocò district, and it is probable that the river Pinto was one of the tributaries of the San Juan. The term **platinum** ultimately crystallized from all these appellations.

E. Milly said that platinum is not an element, but rather an alloy of gold, iron, and mercury; and G. G. L. de Buffon, that it is an alloy of gold and iron. These hypotheses were not acceptable to M. Blondeau, and L. B. G. de Morveau. The observations of W. Lewis, T. Scheffer, A. Cronstedt, A. S. Marggraf, P. J. Macquer and A. Baumé, T. Bergman, T. Willis, C. von Sickinger, L. Crell, C. L. Berthollet and B. Pelletier, A. von Mussin-Puschkin, L. B. G. de Morveau, and J. L. Proust showed that platinum was entitled to rank as an elemental metal, *sui generis*, even though investigators at a later period separated platinum into a group of elements previously unknown.

There have been some erroneous, and some unverified reports of other elements in platina. Thus, G. Osann said that platinum ore from the Urals contains three new metals: *ruthenium* said to have a golden lustre; this unverified ruthenium is not to be confounded with the ruthenium discovered by C. Claus; *polinium*, later shown by G. Osann to be impure iridium; and *pluranium*, shown by G. Osann to be a mixture of silica, zirconia, and titania. C. F. Chandler reported a white metal in native platinum from Oregon which

resembled the white metal found by F. A. Genth in some Californian gold ores. The metal was unnamed, and the reports unverified. S. Kern reported the discovery of a new element in some platinum residues, and he named it *davyum*, but J. W. Mallet showed that davyum is a mixture of iridium, rhodium, and iron. T. Wilm reported a new element in platinum ores, but he did not assign to it a name, and A. Guyard reported an element *ouralium* in Russian platinum, but both reports are unconfirmed. A. del Campo y Cerdan and S. P. de Rubies could detect no new element in the platiniferous minerals from the Urals.

In April, 1803, R. Chenevix[3] received an anonymous circular to the effect that a new metal called **palladium** could be purchased at Forster's of Gerrard Street, Soho, London. The new metal had these properties, amongst others, which showed it to be a noble element previously unknown:

1. It dissolves in pure spirit of nitre, and makes a dark-red solution. 2. Green vitriol throws it down in the state of a regulus from this solution, as it always does gold from aqua regia. 3. If you evaporate the solution you get a red calx that dissolves in spirit of salt or other acids. 4. It is thrown down by quicksilver, and by all the metals but gold, platinum, and silver. 5. Its specific gravity by hammering was only 11·3; but by flattening as much as 11·8. 6. In a common fire the face of it tarnishes a little and turns blue, but comes bright again, like other noble metals, on being stronger heated. 7. The greatest heat of a blacksmith's fire would hardly melt it. 8. But if you touch it while hot with a small bit of sulphur, it runs as easily as zinc.

R. Chenevix believed this was a fraud; he bought up the whole stock; and, after investigating the question, concluded that the substance was not a new element, but rather a platinum-amalgam of peculiar properties. Following the publication of R. Chenevix at the Royal Society, May 13, 1803, where W. H. Wollaston was Secretary, there appeared an advertisement offering a reward to any one who could prepare a grain of this new substance either by R. Chenevix's method, or by any other. No one succeeded in securing the reward, and in 1804, W. H. Wollaston announced that he himself was the discoverer of the new element in platinum ore, and added that he selected the name palladium from the planet Pallas discovered in 1802. It is now difficult to understand why the Secretary allowed the communication of R. Chenevix to be recorded in the transactions of the society. The work of W. H. Wollaston was confirmed by V. Rose and A. F. Gehlen, L. N. Vauquelin, J. B. Trommsdorff, and J. J. Berzelius. The subject was discussed by A. M. White and H. B. Friedman, N. I. Stepanoff, E. K. Fritzman, and M. E. Weeks.

When W. H. Wollaston announced that he was the discoverer of palladium, he also intimated that he had found another new element in platinum ore, and had given it the name **rhodium**—from ῥόδον, a rose—in allusion to the fact that soln. of the salts of the metal have a rose-red colour. The results were confirmed by J. J. Berzelius, and C. Claus. In 1803, H. V. Collet-Descotils, and A. F. de Fourcroy and L. N. Vauquelin announced the existence of two metals in that part of platinum ore which is insoluble in aqua regia; and in 1804, S. Tennant showed that the residues contained two distinct metals, one was named **iridium**—from *iris*, the rainbow—on account of the varying colours of its salts, and the other, **osmium**—from ὀσμή, a smell, or odour—on account of the peculiar, chlorine-like odour of its volatile oxide. S. Tennant first thought of calling osmium *ptenium*—from πτενος, volatile, or winged—in allusion to the volatility of some of its compounds. The chemical relations of these two metals were examined by J. J. Berzelius. As indicated above, G. Osann's report of the discovery in 1828 of three new metals in the platinum ores of the Ural was never confirmed, but C. Claus did find that a residue thought to contain silica, zirconia, titania, and ferric oxide also contained a small proportion of a new metal; he extracted the same metal from the Ural ore, and, following G. Osann, he called the new element **ruthenium**—from Ruthenia, Russia. C. Claus also showed that many of the properties previously ascribed to iridium really belong to a mixture of iridium and ruthenium. The discovery of these four elements was discussed by M. E. Weeks.

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§ 2. The Occurrence of the Platinum Metals

The six platinum metals—platinum, iridium, osmium, ruthenium, rhodium, and palladium—form a group which occur in nature associated together as indefinite alloys, and generally uncombined. Estimates of the percentage elementary composition of the igneous rocks of the earth's crust are considered by F. W. Clarke and H. S. Washington [1] to include platinum $n \times 10^{-9}$, where n is an undetermined integer; iridium and osmium, each $n \times 10^{-10}$; and ruthenium, rhodium, and palladium, each $n \times 10^{-11}$. J. H. L. Vogt gave $n \times 10^{-10}$ for platinum. I. and W. Noddack's estimates are indicated below, and for a later estimate, they gave $5{\cdot}0 \times 10^{-8}$. The subject was discussed by G. Berg, W. Vernadsky, F. Bernauer, A. E. Fersmann, I. and W. Noddack and O. Berg, P. Niggli, E. Herlinger, V. M. Goldschmidt and C. Peters, G. Tammann. O. E. Zvyagintzeff, and P. Vinassa.

Platinum has been reported from extra-terrestrial sources. Thus, J. M. Davison [2] observed platinum and iridium in the meteoric iron of Coahuila, and Toluca, Mexico; H. H. Niniger, in the meteoric iron of Ballinger, Texas; A. Liversidge, in the meteoric iron of Boogaldi, New South Wales; J. C. H. Mingaye also noted platinum in meteoric iron. The subject was discussed by G. Osann, G. P. Merrill, and O. C. Farrington. Later they gave for platinum in meteorites 7×10^{-6}. G. P. Merrill reported the presence of platinum, palladium, iridium, and ruthenium in meteorites; J. C. H. Mingaye, of platinum, palladium, and iridium. Possibly if the platinum metals had been sought in many other meteorites, they would have been found. J. L. Howe said that it is probable all meteorites contain platinum. I. and W. Noddack's estimates for percentages are as follow, atomic distributions are relative to oxygen unity.

	Earth's crust	Igneous rocks	Meteoric iron	Troilite	Atom. distribution
Platinum . .	$8{\cdot}0 \times 10^{-11}$	$8{\cdot}3 \times 10^{-8}$	$1{\cdot}77 \times 10^{-5}$	$3{\cdot}0 \times 10^{-6}$	$2{\cdot}3 \times 10^{-6}$
Iridium . .	$3{\cdot}0 \times 10^{-12}$	—	$2{\cdot}3 \times 10^{-5}$	$5{\cdot}0 \times 10^{-6}$	$3{\cdot}2 \times 10^{-7}$
Osmium . .	$6{\cdot}0 \times 10^{-12}$	—	$8{\cdot}8 \times 10^{-6}$	$1{\cdot}0 \times 10^{-5}$	$1{\cdot}4 \times 10^{-6}$
Palladium .	$8{\cdot}5 \times 10^{-13}$	—	$1{\cdot}9 \times 10^{-5}$	$4{\cdot}5 \times 10^{-6}$	$4{\cdot}6 \times 10^{-6}$
Rhodium . .	$9{\cdot}0 \times 10^{-13}$	—	$5{\cdot}0 \times 10^{-6}$	$1{\cdot}0 \times 10^{-6}$	$1{\cdot}3 \times 10^{-6}$
Ruthenium .	$2{\cdot}3 \times 10^{-13}$	—	$2{\cdot}39 \times 10^{-5}$	$4{\cdot}20 \times 10^{-6}$	$6{\cdot}1 \times 10^{-6}$

C. C. Hutchins and E. L. Holden [3] observed that 16 lines of the platinum spectrum coincide with lines in the solar spectrum. H. A. Rowland, and M. N. Saha classed platinum, iridium, osmium, and ruthenium amongst those elements whose presence in the solar spectrum is doubtful; and palladium and rhodium amongst the elements present in the solar spectrum. The subject was discussed by H. M. Vernon, E. F. Baxandall, J. N. Lockyer, and H. N. Russell. H. von Klüber classes platinum amongst the elements of doubtful occurrence in the fixed stars.

Platinum usually occurs in nature as a native metal alloyed with one or more members of its family, and to a less extent with iron, nickel, chromium, etc. O. E. Zvyagintzeff [4] studied the subject. Some of the native alloys have received special names—*e.g.* native platinum, native iridium, native platiniridium, native palladium, allopalladium, iridosmine—neoyanskite or osmiridium with over 40 per cent. of iridium, and siserskite, or iridosmium, with 30, or less, per cent. of iridium —palladium gold, rhodium gold, and ferroplatinum. Very few compounds of the platinum metals occur as minerals. There are only **cooperite,** represented at first by $Pt(As,S)_2$, and later by PtS; **braggite,** (Pt,Pd,Ni)S; **laurite,** RuS_2, or $(Ru,Os)S_2$; **potarite,** PdHg; **sperrylite,** $PtAs_2$; and **stibiopalladinite,** Pd_3Sb.

In addition to the six members of the platinum family, there may be present iron, copper, gold, etc. Consequently **native platinum** may be host to a number of guests or strangers, and the form of native platinum which is attracted by a magnet, was named by J. F. L. Hausmann *polyxenite*—from πολύς, many, and ξένος, a guest. A. Breithaupt called the latter *sideroplatinum*—from σιδηρος, iron —or simply *ferroplatinum*. A great number of analyses of native platinum have

been reported—by J. J. Berzelius, A. G. Betechtin, S. Bleekrode, M. Böcking, C. Claus, P. Collier, H. St. C. Deville and H. Debray, L. Duparc and co-workers, R. A. Farquharsen, A. Frenzel, F. A. Genth, A. Hadding, G. C. Hoffmann, E. Hussak, J. F. Kemp, S. Kern, I. Koifman, N. von Kokscharoff, M. M. Kositzky, A. Kromeyer, P. Krusch, J. J. Kyle, A. Leplay, W. J. Martin, G. Osann, S. P. de Rubies, S. F. Shemtschushny, L. F. Svanberg, A. Terreil, G. Tschernik, H. N. Warren, and F. Weil. The following is a selection :

	Pt	Pd	Rh	Ir	(Ir,Os)
Colombia	76·82–86·20	0·50–1·66	1·22– 3·46	0·85–2·52	0·95– 7·98
California	76·50–90·24	0·10–1·95	0·65– 3·39	0·85–4·29	0·68–22·55
Canada	68·19–78·43	0·09–0·26	1·70– 3·10	1·04–1·21	3·77–14·62
Urals	68·72–86·50	0·14–1·87	0·30–11·07	0·83–5·32	0·57– 3·85
Australia	59·80–61·40	1·50–1·80	1·50– 1·85	1·10–2·20	25·0– 26·0

The iron ranged from 2·30 to 9·78 ; the copper, from 0·21 to 5·20 ; the gold, from 0·30 to 3·15 ; and the osmium, from 0·19 to 1·13. S. P. de Rubies observed 0·1 per cent. of nickel and cobalt, in some platinum from Kitlim, Urals ; and H. N. Warren found thallium in a number of platinum ores ; and W. F. Seyer found that some concentrates are radioactive. The analyses of **iridium,** and **platiniridium** by L. F. Svanberg were, respectively,

	Pt	Ir	Pd	Rh	Fe	Cu
Burma	19·64	76·85	0·89	—	—	1·78
Brazil	55·44	27·79	0·49	0·86	4·14	3·30

with traces of osmium. Analyses of **osmiridium** or **syserskite** were made by J. J. Berzelius, H. St. C. Deville and H. Debray, C. Claus, O. E. Swjaginzeff and B. K. Brunovsky, P. Kovaloff, and P. A. Wagner. The following is a selection, neglecting small proportions of iron and copper :

	Pt	Ir	Pd	Ru	Os
Colombia	—	57·80	0·63	6·37	35·10
California	—	53·50	2·60	0·50	43·40
Urals	0·62	43·28	5·73	8·49	40·11
Borneo	0·15	58·27	2·64	—	38·94
Australia	—	58·13	3·04	5·22	33·46
South Africa	0·2	17·0	—	8·9	69·9

Analyses of **iridiosmium** or **nevyanskite** were made by H. St. C. Deville and H. Debray, O. E. Swjaginzeff and B. K. Brunovsky, P. Kovaloff, and P. A. Wagner. The following is a selection, neglecting small proportions of iron and copper :

	Pt	Ir	Pd	Ru	Os	Rh
Colombia	0·10	70·40	12·30	—	17·20	—
Urals	1·10	77·20	0·50	0·20	21·00	—
South Africa	0·1–3·1	46·8–77·2	—	0 to 0·5	21·0–49·3	0·5–7·7

The South African iridosmium or nevyanskite contained, in addition to very small proportions of iron, copper, and palladium,

Iridosmium	Ir	Os	Rh	Pt	Ru
Ruthenic	35·5–57·8	33·5–54·4	0–5·7	0–0·6	4·7–8·5
Rhodic	70·0–70·4	17·2–17·3	11·3–17·2	—	—
Platinic	55·2	27·3	1·5	10·1	5·9

According to P. Kovaloff and P. A. Wagner, the so-called **ferroplatinum** of South Africa has 71 to 78 per cent. Pt ; 16 to 21, Fe ; 1·0 to 4·5, Ir ; and 0·2 to 0·8, Pd ; **platinic iron,** 91·85 per cent. Fe, and 8·15, platinum ; **cuproplatinum,** 8 to 13 per cent. Cu ; 70, Pt ; 12 to 15, Fe ; 1 to 2, Ir ; and 0·16 to 0·25, Pd. The **palladioplatinum** has 73 to 84 per cent. Pt ; 3·0 to 21·8, Pd ; and 0·1 to 3·6, Ir. The **rhodioplatinum** has 4·6 per cent. Rh. They also described gold-platinum alloys containing, in addition to very small proportions of iron and copper :

Gold	Au	Ag	Pd	Pt	Ir	Rh
Palladic	86·0–91·1	0 to 4·2	8·2–11·6	0–0·1	—	—
Rhodic	57·0–88·4	—	—	—	—	11·6–43·0
Iridic	62·1	2·1	—	3·8	30·4	—
Platinic	84·6	2·9	—	10·0	—	—

The platinum and iridosmine of commerce is mainly derived from detrital or placer deposits. The colour of native platinum is pale steel-grey, or silver-white (sp. gr. 16·8 to 17·6), or dark grey (sp. gr. 14·2 to 14·3), but sometimes the granules are coated with a black layer of iron oxide, may be magnetic oxide, and in that case, the character of the grains is not easily recognized. It occurs in the form of very fine grains, more or less flattened to form scales, sometimes in the form of irregular nuggets which, as shown by J. F. Kemp,[5] may be or may not be water-worn ; and occasionally, although rarely, small grains show distinct cubic crystallization. The grains of platinum in the Urals are frequently 5 mm. in diameter. A. Inostranzeff, A. von Humboldt, W. Haidinger, A. F. Stahl, G. Rose, and N. von Kokscharoff described larger nuggets—in one case A. A. Lösch described a nugget 2 kgrms. in weight ; W. Haidinger, ore, 5·6 kgrms. in weight ; and three nuggets have been reported from the Nizhni-Tagilsk distinct weighing respectively, 25½ lbs., 21 lbs., and 11½ lbs. The structure of the grains has been discussed by G. B. Sowerby,[6] P. V. Jeremejeff, F. A. Genth, S. Bleekrode, A. Inostranzeff, S. Meunier, A. Liversidge, A. Daubrée, E. Hussak, R. J. Haüy, J. F. Kemp, F. Mohs, B. von Cotta, and R. Beck—*vide infra*, crystals of platinum. B. C. Karpoff found more iron and copper in the outerlayer of native grains than were contained in the nuclei. O. E. Zwjaginstzeff and co-workers discussed the occurrence of rhenium in platinum ores.

Other mineral fragments accompany the platinum granules—*e.g.* chromite, olivine, serpentine, native gold, etc. These minerals are similar to those commonly found in the auriferous gravels and sands, and are doubtless fragments worn away from the rock in which the metals were originally deposited. In the majority of cases, the mother rock, the original home of the platinum, consists of basic or ultra-basic igneous rocks including the peridotites, pyroxenites, and dunites. The peridotites and pyroxenites are composed of iron magnesium silicates, pyroxene, and augite, with hornblende, olivine, chromite, ilmenite, and magnetite ; whilst the dunites consist principally of olivine with some chromite. These rocks have been more or less altered to serpentine. Examples have been quoted by J. F. Kemp,[7] D. T. Day, D. T. Day and R. H. Richards, A. Saytzeff, R. Spring, C. W. Purington, H. Bancroft, L. Duparc, S. Bleekrode, C. Lewis, E. Hussak, F. W. Clarke, A. D. Lumb, P. A. Wagner, and O. E. Zvagintseff and co-workers, J. H. L. Vogt, and L. Leroux.

Throughout the Urals, the primary source of the platinum is the eruptive basic rocks, and the principal outcrops are platiniferous dunite, olivine, gabbro, peridotite, diorite, diabase, and gneiss. The whole of the platinum is derived from gravel deposits which are usually auriferous, and associated with dunite. The subject was discussed by A. Antipoff, R. Beck, A. Bergeat and A. W. Stelzner, F. Beyschlag and co-workers, V. J. Bourdnakoff and J. M. Hendrikoff, C. Bullman, A. des Cloizeaux, A. Daubrée, L. Duparc and co-workers, M. von Engelhardt, J. F. von Erdmann, A. von Ernst, J. Fedoroff, A. Frenzel, M. Gorbatscheff, E. de Hautpick, G. von Helmersen, R. Helmhacker, A. von Humboldt, A. Inostranzeff, P. V. Jeremejeff, A. Katterfeld, J. F. Kemp, N. von Kokscharoff, A. Koltowsky, A. Krassnopolsky, P. I. Krotoff, G. Kunz, A. T. Kupffer, A. Laurent, M. Leplay, F. Loewinson-Lessing, A. A. Losch, H. Louis, M. Lubarsky, J. Menge, S. Meunier, A. Minchin, R. Murchison, J. W. Muschketoff, C. W. Purington, G. Rose, S. P. de Rubies, W. Sapelkin and M. Iwanoff, A. Saytzeff, M. Sivkoff, A. F. Stahl, J. N. Fuchs, M. Teploff, A. Terreil, M. Tschupin, W. L. Uglow, W. Vernadsky, N. K. Wyssotsky, A. Zawaritsky, and C. Zerrenner.

A. Daubrée pointed out the constant association of platinum with olivine rocks and chromite, and emphasized the resemblance of these rocks to meteorites ; and S. Meunier argued that the platinum and iron of these rocks are not magmatic, but were introduced as chlorides and afterwards reduced by heated hydrogen. E. Hussak thought that the platinum found its way into these rocks by the decomposition of pyrites containing platinum—*vide infra*. C. Bullman objected to

hypotheses, like that of L. Hundeshagen, based on the precipitation of platinum from soln. because of the insolubility of the metal. A. Inostranzeff inferred from the occurrence of platinum in the serpentine, olivine, and chromite rocks that the platinum metals crystallized first from the original molten magma; and the subject was discussed by F. Beyschlag and co-workers, and R. Beck.

When present in serpentine, platinum is commonly disseminated throughout the rock in fine particles—seldom in bodies. Platinum occurs in sedimentary and metamorphic rocks—*e.g.* sandstones. The platinum in sedimentary rocks is usually associated with quartz, copper, nickel, silver, and palladium, whilst in alluvial deposits, it is associated with chromite, magnetite, ilmenite, iridium, and osmiridium. Examples of the occurrence of platinum in these rocks were discussed by R. Beck, F. Beyschlag and co-workers, S. Bleekrode, J. B. J. D. Boussingault, C. Bullman, L. Hundeshagen, E. Hussak, J. B. Jaquet, A. Karpinsky, J. F. Kemp, A. Krassnopolsky, P. Krusch, J. C. H. Mingaye, J. S. Newberry, F. Sandberger, R. Spring, and P. A. Wagner. There are a few occurrences of platinum in quartz veins—*e.g.* the cases discussed by J. B. Bell, P. A. Wagner and T. G. Trevor, and R. A. Farquharson.

Platinum has been found in many sulphide ores and in metals derived from those ores. O. E. Zvjaginsteff and A. N. Filippoff [8] studied the subject. E. Gueymard observed it to occur in tetrahedrite; H. Vogel, in the metal ores of Boitza, Transylvania; H. L. Wells, W. E. Hidden, W. E. Hidden and J. H. Pratt, in the sulphide—nickeliferous pyrrhotite, and chalcopyrite—ores of Sudbury, Canada; J. H. L. Vogt, and G. Lunde and M. Johnson, in the nickeliferous pyrrhotites of Norway; W. N. Hartley and H. Ramage, in pyrites; W. Baragwanath, and C. W. Dickson, in chalcopyrite; F. W. Clarke and C. Catlett, in polydymite; H. L. Wells and S. L. Penfield, W. C. Knight, J. F. Kemp, S. F. Emmons, and T. T. Read, in covellite; R. W. Brock, in the sulphide bearing quartz of British Colombia; J. Catharinet, in the pegmatite of Copper Mountain, British Colombia; J. C. H. Mingaye, in the sulphide ores of Broken Hill, New South Wales; F. W. Clarke, A. Knopf, and L. A. Palmer, in plumbojarosite; F. A. Genth, in some copper-lead-iron sulphides of Lancaster Co., Pennsylvania; and M. d'Argy, in galena.

P. Krusch [9] reported platinum in graywacke; A. Orio, in mica schist; J. B. Jaquet, in silurian shales; F. Sandberger, in limonite; A. Eilers, in blister copper; A. Cissarz, in Mansfeld copper shales; J. F. Kemp, in stanniferous sands; J. L. Beeler, in silver ore; G. C. Hoffmann, in a silver amalgam from Vital Creak, British Columbia; M. Pettenkofer, and E. Priwoznik, in some gold coins; H. Rössler, in silver bullion; F. Mylius and C. Hüttner, C. Palmstedt, and H. S. Schrewsbury, in some coins; G. Lunge, in bessemerized nickel; A. L. Day and R. B. Sosman, in electrolytic nickel; A. Daubrée, nickel in platinum; M. von Leuchtenberg, in commercial copper sulphate; J. G. Rose, in commercial borax which had been fused in platinum vessels; G. Lunde, in basic rocks, and tantalite of Finland—0·000006 per cent.; G. Lunde and M. Johnson, peridotite, 0·000074 per cent.; serpentine, 0·00003 per cent.; and chromite, 0·000128 to 0·0020 per cent.; and V. M. Goldschmidt and C. Peters, and K. Hélouis, in coal. W. F. Seyer found the platinum concentrates of British Columbia are radioactive.

The amount of platinum in country rock is generally so small that the commercial extraction of the metal is out of question. Although native platinum has been reported from many, widely-scattered localities, the districts which produce the metal in commercial quantities are few in number, and limited in extent.[10] The geographical distribution of the metal is summarized in Fig. 1.

Europe.—There is no deposit of platinum of any commercial value in the **British Isles.** R. P. Greg and W. G. Lettsom [11] reported that the presence of platinum has been recognized at Fort Regent, Jersey, and at Buittle, Kirkcudbrightshire; L. de Launay, at Hormor Hill, Shropshire; E. H. Davison, in the Lizard district, Cornwall; and J. W. Mallet, in the auriferous sands of Wicklow, Ireland. Platinum is not worked in **France,** but there are a

few places where its presence has been reported. G. A. Kenngott [12] announced its presence at St. Arey, Dépt. Isère; and E. Gueymard, at Chapeau in the Vallée du Drac, at Rousses in Oisans; and near Presles in Savoy. J. J. Ebelmen, and E. Gueymard noted that platinum is associated with many of the minerals in the Alps. P. Berthier and A. C. Becquerel, M. Villain, and M. d'Argy mentioned the occurrence of platinum in the galena of Confolens, Alloué, Epénéde, Meller and Plauveille, although M. Dangez, and H. F. Gaultier de Claubry expressed some doubts of the reports. J. F. Kemp mentioned its occurrence in the stanniferous sands of Morbihan. In **Germany**,[13] the presence of platinum has been reported in the auriferous sands of the Rhine by L. Hopff, and J. W. Döbereiner; in the silver of Commern and Mechernich, by H. Rössler; in the gold of Wilhelmshütte, by J. J. Berzelius; and near Tilkerode, and Zorge in the Harz, by F. Wrede, J. C. L. Zincken, and O. Luedecke. According to P. Krusch, platinum occurs finely disseminated in the slates and graywackes of Westphalia—Freudenberg, Siegen, Meschede, Sauerland, and Westerwald. The question whether a profitable extraction can be made has been seriously considered. Traces of platinum have been reported in the auriferous sands of Olahpian, and at Boicza in the Siebenbürgen, in **Rumania**, by W. Haidinger,[14] V. von Zepharovich, J. Molnar, C. Zerenner, P. Partsch, A. Patera and B. Kopetzky, and J. H. Vogel.

According to B. N. Menschutkin,[15] indications of the existence of platinum in **Russia** were first obtained in the gold-placers of Ekaterinburg (since 1918, Sverdlovsk), Eastern Siberia. Analyses showed it to be osmiridium; and in 1824, it was found north of

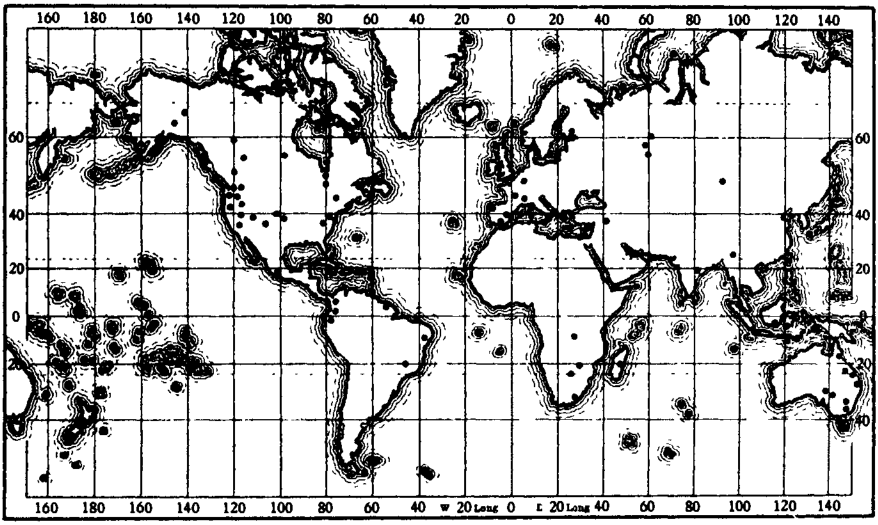

FIG. 1.—The Geographical Distribution of the Platinum Metals.

Ekaterinburg, and declared a state monopoly. About 1914, Russia was producing about 93 per cent. of the world's supply of platinum. The metal was derived from the extensive deposits of alluvial sands in the Ural Mountains. According to C. Claus, A. Köppen, A. Katterfield, N. Mamyscheff, and N. von Kokscharoff, small quantities of a greyish-white, metallic substance was observed in the gold washings of Verk-Isetsk in the Siberian Urals; but the grains were not recognized as platinum until 1822. The development of the Nizhni-Tagilsk deposits began in 1824, and in 1825, the metal was also found in Goroblagodat. The most prolific producing districts are south-west of Nizhni-Tagilsk, north-west of Nizhni-Turinsk, and the Isoff district, near Goroblagodat. The whole of the platinum is derived from gravel deposits which are usually auriferous and associated with dunite. According to N. K. Wyssotsky, and A. D. Lumb:

The platiniferous belt of the Urals consists of four parallel bands striking, roughly, north and south; the westernmost of these, made up of crystalline schists, forms the watershed between Europe and Asia. The next band to the east comprises olivine- and mica-gabbros, diallage-peridotites, diorites and altered syenites—all of which have been erupted from a great depth. The third band is made up of Lower Devonian sedimentary rocks, shattered and buried in places by diabasic eruptive rocks. The eastern portion of this band is formed of eruptive rocks of deep-seated origin which may be gneissose granites. The fourth, or most easterly band, is composed of ancient rocks, which have been eroded by the advancing sea of Lower Tertiary age. The area emerged from the waves as early as the Carboniferous period; consequently the accumulation of platinum, and in some localities of gold, in the

surface-deposits, were not swept away. They were concentrated later on in the alluvia—perhaps at the time of the most intense glaciation, probably in the Pleistocene.

The basic igneous rocks, from which the platinum is derived, are exposed in the form of discontinuous elliptical outcrops near the summits of the Urals, particularly on the western side of the mountains. These outcrops attain larger dimensions in the northern and central Urals than farther south. The process of concentration of platinum in the gravels has clearly extended over a very long period of time, and it is probable that the richer gravels have been reconcentrated, perhaps several times.

According to L. Duparc and co-workers, the deposits are essentially of magmatic origin. The structure of the rock is in the nature of concentric bandings; the felspathic rocks at the outer edge gradually grade into the intermediate stage of pyroxenes, until the central dunite is reached, composed of olivine and chromite. The richness of the gravels is in proportion to the size of the dunite deposits, and to the extent of erosion of these rocks. Platinum ore derived from a pyroxenite source usually contains high percentages of platinum and palladium, but low percentages of osmium and iron. The reserves in 1916 were sufficient for about twelve years, provided that the same methods of working and rate of extraction were employed during that period.

According to A. D. Lumb, platinum is concentrated in channels of the Rivers Iss, Veeya, and Tura; north of these, the metal is obtained from beds of the Rivers Sognovki, Kythymi, and Mala Kosva; and, along with gold, in the systems comprised in the Rivers Vagran, Lobva, Niasma, Liabia, Aktai, Emerlo, Talits, and Ivdovi. In the south, platinum is worked on the tributaries of the Rivers Tagil, Salda, Imiaum, and Tura. In the Nizhni-Tagilsk district, the richest placers are in the valleys of the Rivers Visim, Martian, Sisim, Chaush, and Cherna, and farther south, along with gold, in the gravels of Nevian, Verkhne-Iset, Bilenibaev, Alapaev, Sysert, Kyshtym, and Mias, and in the Rivers Tanalyk, Sakmar, and Urtazym. There are smaller deposits in Nikolae-Pavdinsk, Rastes, and Systersk. The placer deposits are derived from country rock made up of serpentine gabbro, diallage, and olivenite and the associated minerals are chiefly quartz, zircon, ilmenite, chromite, magnetite, spinel, and native gold and palladium. The crude platinum usually includes iridium, rhodium, ruthenium, and iron. A. A. Losch, A. Karpinsky, and A. Krassnopolsky discussed the occurrence of platinum in Bissersk, where a 2-kgrm. nugget of platinum was found. In addition to what has been previously stated, the Ural deposits were discussed by C. Blömeke, G. Rose, A. Inostranzeff, I. Koifman, A. G. Betechtin, V. P. Mishin, G. Padalka, E. P. Moldavantzeff, P. P. Pilipenko, G. A. Dodonoff, A. Breithaupt, A. N. Zavaritzky, J. J. Berzelius, C. Zerrenner, A. von Lasaulx, P. V. Jeremejeff, G. Schüler, F. Beyschlag and co-workers, A. F. Stahl, M. von Engelhardt, J. Fedoroff, D. Serdyuchenko, and C. Hintze—*vide supra*. A. Solitander reported the presence of platinum in the auriferous sands in the north of **Finnland.**

The occurrence of traces of platinum in the auriferous sands of the River Ivalo, in **Lapland**, was noted by A. E. Nordenskjold,[16] and F. J. Wiik, and at Vasko, and Tanna-Juk, by J. H. Langer. The occurrence of traces of platinum in the nickeliferous pyrrhotite of Småland in **Sweden** was discussed by J. H. L. Vogt,[17] L. de Launay, and F. M. Stapff. J. H. L. Vogt,[18] and G. Lunde and M. Johnson also described the presence of traces of platinum in the nickel ores of **Norway**; and G. vom Rath, in the silver of Konigsberg. J. H. Vogel [19] reported traces of platinum in **Portugal.** According to L. N. Vauquehn,[20] platinum occurs in **Spain** in the silver mines of Guadalcanal, Estremadura, although J. J. Berzelius had doubts on this subject. A. Orio reported traces of platinum to be associated with the pyrites of Asturia. According to A. D. Lumb, the metal has also been noted at Ronda, Malaga, in the alluvial deposits along the Rivers Verde and Guadaiza. The deposits are derived from serpentine and peridotite rocks. The pay gravels contain 8 grms. of platinum per ton. The metal has also been reported in the other parts but not in payable quantities. It occurs principally in the northern districts, and in the Rivers Minho, Luna, Sil, Orbigo, Gallego, Cinca, Darro, and lower Jenil, where it occurs in the concentrate sands accompanied by magnetite, ilmenite, zircon, and frequently gold. S. P. de Rubies, E. Rubio, L. Duparc and A. Grosset, T. C. Earl, F. Gillman, and D. y Orueta and S. P. de Rubies discussed the occurrence of platinum in Spain.

Asia.—The Uralian deposits in Asia have been indicated in connection with the Russian deposits. R. Helmhacker [21] reported the presence of platinum in the auriferous sands of **Altai**; and it has also been reported in **Armenia**—Batum and Sasun—by L. de Launay,[22] but none was found by A. G. Betechtin in the peridotites of Gokoha. J. F. Kemp, and N. Nakovnik reported it in **Siberia**—in Baikal, Balkash, and Jenissei. K. Jimbo, and T. Wada observed that in **Japan,** the metal occurs in the auriferous sands of the province of Ishakari, and the Yubari River of Iburi; in the Rivers Yubari-garva, Pechau, and other rivers in the province of Hokkaido where gold and iridosmium are associated with the platinum. It is also found in the gold and iron sands of the Nishi-Mikawa, in the province of Sado. E. de Hautpick mentioned the occurrence of platinum in the auriferous gravels in the Uryanchai district of Mongolia, on the Russian border of **China.** L. de Launay found that the metal also occurs in the auriferous sands of Rigal, in the **Philippines.** Traces

of platinum have been noticed associated with the gold obtained from native workings at Bonai, in **India.**[23] Platinum, and iridioplatinum were discovered in **Burma,** in 1831, in the auriferous sands of the Ava. The occurrence was described by J. Prinsep, A. Faber, R. Romanis, and H. Burney; and M. F. Heddle proposed to call the metal from this locality *avaite*. Platinum occurs associated with gold in the Irawaddy River, and it has been obtained commercially at Myitkyina; and it has been located in the iridosmium in the auriferous gravels of the rivers draining the Patkoi Ranges on both the Assam and the Burma sides. Platinum was also discovered in south-eastern **Borneo** in 1831, in the gravels of Gunung Lawack; and, according to T. Posewitz,[24] it is now obtained as a by-product of the gold-washing in the province of Tanah-Laut. The platinum is here associated with osmiridium, and gold. The mineral laurite, $(Ru,Os)S_2$, occurs in these deposits. L. Hundeshagen also described the occurrence of platinum in the diamond placers, west and south-east of Borneo. The Borneo platinum was examined by M. Böcking. According to L. Hundeshagen, platinum occurs in **Sumatra** at Singenggnu, east of Sipongi, along with gold, wollastonite, and grossularite in limestones and schists near intrusions of grano-diorite and augite-diorite. E. Heurteau discussed the platinum occurrences in **New Caledonia.**

Africa.—G. Aimé [25] observed traces of platinum in the galena of **Algiers**; E. Ackermann, in grains in a creek at Gondoko, and at Missiva in the **Sudan** and Upper Senegal; L. Duparc, L. Duparc and E. Molly, and F. Hermann and O. Günther, in Birnir, **Abyssinia**; N. R. Junner, in **Sierra Leone**; R. P. Rothwell, in the bed of the River Uelle, in the Katanga district in the **Congo Free State**; and A. Lacroix, as a by-product in the alluvial gold mining on the Vatana River, near Ambia, in **Madagascar.** Traces of platinum have been also reported in the auriferous gravels of Fenerive, Marolambo, and Vandrozo, in Madagascar. The subject was discussed by L. Duparc, and L. Duparc and co-workers. The gold-platinum deposits at Ruwe, in **Katanga,** were described by P. V. Brande.

A. E. V. Zealley [26] located platinum in the conglomerates and gravels of the Somabuba Fields, near Gwelo, in **Rhodesia.** The country rock is serpentinized dunite. The deposit is capped by a ferruginous, siliceous gossan. The ore yields 3 ozs. 12 cwts. of platinum per ton, and 7 ozs. of osmiridium per ton. B. Lightfoot, and H. B. Maufe also noted gold and platinum in a reef in the great dyke of norite at the head of the valley drained by the River Umtebekwe. The platinum is found only in notable quantities in those areas of the dyke where felspar-rich norite is present. According to P. A. Wagner, there are large reserves of platinum in South Africa, principally in the **Transvaal.** The platinum metals occur in the most diverse circumstances, and in rocks ranging in geological age from the most ancient to the most recent. W. Bettel noted the metal in the black sands from the battery "clean-ups" on the Rand at Klerksdorp, and other gold-mining districts, and in the residual slimes at the Rietfontem mines. A. Hall and W. A. Humphrey observed that samples of chromite from Kromdaal, near Rustenburg, and from the Secocoeniland deposits may contain 1 to 1½ dwt. of platinum per ton. The platinum metals in the Transvaal occur in the ultra-basic and basic rocks about Uitkomst, Preezburg, and Messma; in the auriferous conglomerates of Witwatersrand, and the Black Reef in Klerksdorp district; in the norite zone of the Bushveld; and in the igneous complex—a vast body of plutonic and volcanic rocks in the central part of the Transvaal. According to P. A. Wagner, the platinum here occurs in

I. Oreumotectic deposits formed by segregation from the parent norite magma, and occurring in the acid quartz-bearing differentiates of the norite magma.

II.—Orthotectic deposits formed by direct segregation from the parent norite magma.

A.—Deposits in which platinum is associated with magmatic nickel-copper-iron sulphides in norite, pyroxenite, and harzburgite.

(*a*) In the upper part of the norite zone, *e.g.* (i) Deposits of the Blaauwbank type in which the ore-bearer is quartz-bearing anorthositic norite. (ii) Deposits of the Stulpoort Park type in which the ore-bearer is a medium grained, spotted norite rich in felspar. (iii) Deposits of the Minsk's Claims type, Lydenburg District, in which the ore-bearer is a rather coarse-grained diallage norite rich in felspar.

(*b*) In the lower part of the norite zone, *e.g.* (iv) Deposits of the Merensky Horizon type occurring above and below the main horizon in the Lydenburg District. (v) Deposits of the Merensky Horizon type as developed in the Rustenburg, Pretoria, Lydenburg, Pietersburg, and Potgietersrust districts; the ore bearers are pseudo-porphyritic pyroxenitic diallage-norite, felspathic, pyroxenite, felspathic harzburgite and chromitite. (vi) Deposits of the Tweenfontain type, Potgietersrust District in which the ore-bearer is a fine-grained pyroxenitic diallage-norite emerging into coarse-grained felspathic bronzitite and bronzitite. (vii) Deposits of the Valk fontein type, Rustenburg District, in which the ore-bearer is bronzitite.

B.—Chromitite deposits.

C.—Olivine-dunite deposits; iron-rich olivine-dunite deposits and hortonolite-dunite deposits.

III.—Contact metasomatic deposits in altered dolomite or sheared banded-ironstone directly underlying platinum-bearing norite or pyroxenite.

P. A. Wagner and T. G. Trevor described the platinum deposits in the Waterberg District; F. Behrend, the Transvaal occurrences. J. G. Rose, A. L. du Toit, P. A. Wagner, and W. H. Goodchild discussed the platinum in the magmatic copper-nickel deposits of Insizwa, and Tabankulu in Griqualand, **Cape Province.** V. Hartog established the presence of small amounts of platinum in the kimberlite of all the more important South African diamond pipes at Kimberley, Blumfontein, Wesselton, Jagerfontein, Premier, De Beers, and Du Toits. The South African deposits were discussed by L. Duparc and M. Tikonowich, H. Merensky, H. R. Adam, A. Newberry, M. Lipovsky, E. Reuning, J. H. L. Vogt, and P. Kukuk.

North America.—In **Canada,**[27] platinum and iridium was reported by T. S. Hunt in the gold washings of the River Loup in *Quebec,* and the occurrence in Quebec, and East Canada was mentioned by J. F. Kemp, and J. F. Donald. E. R. Faribault discussed the occurrences in *Nova Scotia;* and G. P. Howley, in *Newfoundland,* where traces occur in the serpentinized area in the region of Mount Cormack. Platinum is associated with the copper-nickel ores at Sudbury in *Ontario,* and in the extraction of nickel, the platinum accumulates in the matte from which it is commercially extracted. D. E. Roberts and R. D. Longyear found a mean content of 0·0068 oz. of platinum, 0·022 oz. of gold, 0·223 oz. of silver, per ton in addition to 1·95 per cent. of nickel, and 1·11 per cent. of copper. The subject was discussed by F. W. Clarke and C. Catlett, A. P. Coleman, H. J. L. Vogt, and J. W. Dickson. Platinum has been also reported from the vicinity of Star Lake, and Le Pas district in *Manitoba.* G. C. Hoffmann reported platinum in the sands of the North Saskatchewan River, near Edmonton, *Alberta.* The subject was discussed by C. Camsell. Several occurrences of platinum associated with gold have been reported in *British Colombia.* Thus, G. C. Hoffmann, J. F. Donald, J. F. Kemp, and C. Camsell found it in the River Tulamsen and its tributaries—Slate, Cedar, Eagle, Bear, and Granite Creeks. W. L. Uglow observed platinum at Franklin Camp near Grand Forks, and it has also been reported on the Mother Lode Claim, Burnt Basin; and in the following localities—Kootenay, Tranquille, Frazer, North Thompson, and Clearwater Rivers; Rock, and Siwash Creeks; and Yale District.

Many occurrences of platinum have been reported in the **United States.**[28] According to C. Bullman, it occurs in *Alabama* in small quantities; and in *Alaska* platinum occurs as a by-product in the treatment of copper ore at the Salt Chuck Mine, Ketchikan; the placer deposits of Dymo, Bear, Sweepstake, and Boob Creeks have furnished some platinum. The metal also occurs near the Red Mountain, Kenai Peninsula; and at the head of Kasaan Bay, Prince of Wales Island. These deposits were discussed by G. C. Martin and co-workers, and D. G. Campbell. W. P. Blake, and J. F. Kemp described occurrences in *Arizona.* The occurrence of the platinum metals in *California* has been discussed by B. Silliman, R. M. Patterson, C. L. Henning, W. F. Clarke and C. Catlett, W. P. Blake, J. D. Dana, H. Dubois, C. Blömeke, J. E. Teschemacher, H. Ludwig, F. Weil, J. F. Kemp, and O. Luthy. The metals, associated with gold, as the dominant metal, occur over a wide area in placer deposits. The platinum is found in auriferous sands from streams rising in the belt of serpentine rocks in the Siskyou, Butta, Calaveras, Stanislaus, Trinity, Yuba, Kern, Humboldt, Plumas, Sierra, Placer, Shasta, and El Dorado Countries. The platinum in the foothills of the Sierra Nevada was in old stream channels on the western slopes of the mountains. Platinum occurs in the beach deposits on the Pacific coast in the counties of Coos, Curry, Josephine, Oregon, and Del Morte. There is some alluvial platinum near Placerville. The Californian platinum contains 25 to 45 per cent. of iridium, and it is believed to originate in the serpentine and olivine rocks of Sierra Nevada, etc. J. D. Dana mentioned the occurrence of platinum in the Klamath region; and F. A. Genth, at Capo Blanco. Platinum was reported by J. F. Kemp to occur in *Colorado,* in the black sands of Clear Creek; in the gold gravels of Como; and in a vein near Villa Grove. J. F. Kemp also reported platinum to occur in the Lumpkin county in *Georgia;* and J. F. Kemp, and T. H. Hite, in the auriferous sands of Snake River from Baskerville to Lewiston in *Idaho.* In *Montana,* J. F. Kemp noted the occurrence of platinum at Miles City; and W. Browne, in the auriferous sands of Warm Springs near Helena. In *Nevada,* J. L. Beeler mentioned the occurrence of platinum in the silver ore at Austin; and W. W. Attwood in the gold of the Comstock Lode. Platinum is associated with the copper-nickel- and cobalt-sulphide ores from Key West, and the Great Eastern Mines near Bunkerville, Lincoln Co. According to F. A. Hale, and A. Knopf, platinum is extracted with the copper and gold ores of the Boss Gold Mine, and the Oro Amigo Mine, near Goodsprings, Clark Co. In *New York State,* P. Collier noted that platinum occurs at St. Lawrence near Plattsburgh; and J. M. Clarke, in alluvial sands of the Adirondack region. In *North Carolina,* platinum was reported by J. F. Kemp to occur in the sands of the Cowee Creek, Maron Co.; by C. U. Shepard in the gold washings of Rutherford and Burke counties; at Mason Mountain, Mason Co.; at Brown Mountain in Burke; and at Burnsville, Yancey Co. W. E. Hidden, F. A. Genth, and F. P. Venable also discussed the reports of these occurrences. In *Oregon,*

platinum was reported by J. F. Kemp, C. Bullman, R. P. Rothwell, J. V. Thévenet, A. E. Kellogg, C. L. Henning, W. P. Blake, and C. F. Chandler to occur in auriferous sands of the Rogue River; in the auriferous sands of Port Orford and Ecklay, Curry Co.; at Kirkby, Josephine Co.; in the beach deposits near Bullards, and Marshfield; in the placer deposits of the Waldo district; in streams from the Blue Mountains, eastern Oregon; in the Granite and Canyon districts; and in the Spanish Gulch, Wheeler Co. Platinum has been reported in *Pennsylvania* by G. A. Kenngott; by F. A. Genth, and J. F. Kemp, associated with the sulphide ores in the mica-schist of Lancaster Co., and in the black triassic shales of Boyertown. In *Washington*, J. M. Clarke, and J. T. Pardee noted the extraction of small quantities of platinum from the beach deposits near Yacolt, and south of the Straits of Juan de Fuca. It has been also located in the Cascade Mountains in the centre of the State. J. M. Hill reported platinum and gold in *Utah* in the Green River east of Vernal, and in the Colorado River, near Hite. According to T. T. Read, J. F. Kemp, S. F. Emmons, C. L. Henning, and H. H. Taft, platinum and palladium (1 : 3) are obtained in *Wyoming* from the Rambler Mines in Albany Co. F. L. Hess discussed the occurrence of platinum on the Centennial Ridge, Wyoming.

C. F. Landero,[29] in his catalogue of the minerals of **Mexico**, did not mention the occurrence of platinum in that country although H. J. Burkart, E. von Hautpick, G. von Uslar, and J. J. Nicholl, reported its occurrence in the vicinity of Xacala in the state of Hidalgo; J. F. Kemp, in the Yedras Mine in Smalva; and E. von Hautpick, in the state of Guerrero. J. D. Dana reported the occurrence in Choloteca and Gracias in **Honduras**; L. B. G. de Morveau, and L. N. Vauquehn discussed the occurrence of platinum in the auriferous sands of the River Jaky of **San Domingo**; and the subject was discussed by M. Percy, A. F. Gehlen, and A. Vogel, L. N. Vauquelin, L. B. G. de Morveau, and A. von Humboldt.

South America.—Reports on South American platinum were made at the end of the seventeenth century, or the beginning of the eighteenth century, by T. Bergmann,[30] M. R. de Celis, A. F. Gehlen, A. von Humboldt, W. A. Lampadius and G. P. Plattner, A. Damour, and W. Thomson. Before 1914, **Columbia** was the second largest producer in the world. J. B. J. D. Boussingault mentioned the occurrence of platinum at Santa Rosa de Osos in Antioquia; A. von Humboldt said that the reports of its occurrence at Bolivar are not true; L. de Launay reported platinum in Certegui. The principal source of supply is the alluvial deposits at the head of the San Juan River, where it enters the Pacific Ocean, north of Buenaventura, particularly tributaries of this river—the Condato, Platina Cajon, Opagado, and Tamanal Rivers; and the metal is also obtained in the Upper Atrato River which flows into the Caribbean Sea. The area including the watersheds of the San Juan and Upper Atrat Rivers is known as the Choco district. The metal found in the gravels of the San Juan River is associated with about an equal proportion of gold, but the gravels of the Atrato River have about 15 of platinum to 85 of gold. Early in the nineteenth century, the platinum had so low a commercial value that a great proportion was rejected as waste in the operation of refining gold by the dry-blowing system. Later, as platinum increased in value, much of the dumped metal was recovered— notably in Quibdo, the capital of the Choco district. T. Ospina discussed the gold and platinum deposits in the Mira River; and deposits also occur in the Micay River, in the Barbacoas district. I. Domeyko reports the occurrence of platinum in the departments of Novita and Citara; it occurs in the province of Lloro, and other places discussed by R. W. White, H. Heuland, G. von Humboldt, G. J. Kellner, and A. D. Lumb.

B. L. Millar and J. T. Singewald [31] reported that platinum occurs associated with gold in **Ecuador** in the area covered by the Rivers Bogota, Cachabi, Uimbi, Santiago, and Coyapas. The deposits are of no great economic importance, and operations are mainly confined to native washings. A. Damour, and E. D. Levat reported that platinum is associated with auriferous sand in the River Aporuague, in **French Guiana.** L. J. Spencer [32] described the platinum found in the diamond washings of **British Guiana.** C. Blomeke reported that platinum occurs in **Peru** in the states of Rita, Lucia, Iro, and Aporto. J. J. Kyle, and J. Corréa reported platinum to occur in the auriferous sands of Tierra del Fuego, **Patagonia.** It occurs in the serpentine of Alta Gracia, Cordoba [33]—**Argentina.**

In 1801, J. Vieira do Couta [34] reported that platinum occurs in **Brazil** in the sands of the Lages River, near Conceiçao, Minas Graes; and E. Hussak observed that the platinum is confined to the alluvium of the rivers having their rise on the eastern slope of the Serra do Espinhaco—the Rio Tanque, Rio Itambe, Rio Peixe, Rio Antonio, and Rio Gyanhaes; and at Condalo, farther north, its occurrence was described by W. H. Wollaston, J. Mawe, and E. Hussak. A. von Humboldt, and E. Hussak reported that platinum also occurs associated with gold and diamonds at Cornego, and in the Rio Abaeté, Minas Graes. E. Hussak described occurrences at Fazenda Condado in Corrego do Bom Successo; in the State of Parnahyba do Norte in the gold washings of the Rio Bruscus; in the gold-bearing jacutinga of the Gongo Socco mine; in the south of the Serra, Itacolumy; and in the alluvial gravels of the Cuyaba and Coxim Rivers south of Matto-Grosso. G. Leonhard, and I. Domeyko also noted platinum in the diamond deposits of Matto-Grosso. L. F. Ferraz observed it in the gold-dredgings of the Rio Coxipo-Mirim. A. J. de Sousa Carneiro reported platinum in the State of Bahia, in Ituassu, Feira de Sao Anna, Serra do Assurura, Sao Bartholomeu, and in the Serras do Pitango and Macahubes. Reports

were made in the first half of the last century on the Brazilian platinum by A. F. Gehlen, J. B. J. D. Boussingault, and S. J. Denis.

Australasia.—In *New South Wales*,[35] platinum is obtained at Platina in the Fifield district, and the occurrence was described by J. B. Jaquet, B. Dunstan, J. Plummer, and A. D. Lumb; the metal also occurs in the beach sands on the coastal border of New South Wales and Queensland near Ballina, at Evans Head, and at Currumbim. J. C. H. Mingaye, and J. B. Jaquet described the occurrence in the Broken Hill district at Little Darling and Mulga Springs Creek. Here the deposits resemble those of Sudbury, Canada. B. Dunstan, and L. E. Ball described the occurrences of platinum in *Queensland*, where it occurs in the beach deposits between Southport and Currumbin; in the Coopooroo and Wairmaba Creeks, near Innisfail; in the Lucknow and Alma reefs of the Gympie goldfield; in the auriferous, alluvial deposits of Brickfield Gully; and at the head of the Don River, Central Queensland. A. D. Lumb, and A. M. Howitt described the occurrence of platinum in *Victoria*, at the Walhalla Copper Mine, and in the Thompson River Copper Mine. According to R. Beck, and A. D. Lumb, platinum and iridosmium occur in *Tasmania* in the Bald Hill district near Waratah; in the placer deposits of the Nineteen Mile Creek and its tributaries—Linger-and-Die, McGinty's and Barren Creeks; in the rivers Heezleword, Whyte, Castray, Huskisson, Wilson, Boyes, and Savage, and at the Badger gold diggings, west of Savage River, and at the Salisbury goldfield, near Beaconsfield. Platinum has been reported near Boolcoomatta in *South Australia*; and also in *Papua* in the Lakekamu district, and in the Yodda Valley.

Platinum is obtained in *New Zealand* from the Orepuki district in Southland. The subject has been discussed by R. A. Farquharson, J. A. Pond, L. de Launay, R. Beck, and A. D. Lumb. The presence of platinum has also been reported in quartz bodies near the Thames River, and in a pyritic body near the Taramekan River in Westland; in the Taraka and George Rivers flowing into Awarua Bay; in the beach sands of the east coast of Otago; in the Clutha River; in the Nelson gold district; and in the Parapara district.

The world's production of platinum [36] is about 9 tons per annum, and when averaged per annum for the six years ending December 31, 1914, and expressed in troy ounces, it was as follows:

Russia	Colombia	Australasia	United States	Borneo Sumatra	Burma	Canada
200,000	12,080	790	594	180	46	33

The Russian industry was so disorganized during the war and the revolution that the output from the Urals dropped from 210,000 troy ozs. in 1912 to 5500 troy ozs. in 1921. Colombia and Canada accordingly increased their outputs, and South Africa started producing the metal. The Uralian output is recovering its place, for it again leads, with Colombia, and South Africa respectively, in the second and third ranks. The world's production approximated:

	1915	1919	1925	1926
Australia	43	162	436	—
Canada	475	690	8,698	9,521
Colombia	18,749	32,236	56,000	55,000
Russia	104,000	39,425	94,800	92,700
South Africa	—	—	—	4,951
United States	1,190	10,460	4,325	4,923
Total	219,933	72,513	164,259	167,500

The production of platinum in Russia was discussed by P. Krusch, P. V. Shchuka, C. Bullman, A. de Keppen, L. de Launay, L. Duparc, and C. Blömecke; in Colombia, by C. Bullman, and L. de Launay; in South America, by C. Blömecke; in Canada, by C. Bullman, J. F. Donald, and L. de Launay; in the United States, by P. Krusch, C. Bullman, and J. F. Kemp; in Sumatra, by P. Krusch; and in Borneo, by L. de Launay, and P. Krusch.

According to J. L. Howe, no reliable data have ever been available for the production of platinum because much of the Russian output has intentionally not been reported in order to avoid taxes. However, with the available data he estimated the upper and lower limits of the amounts of platinum produced in the world up to January, 1917, in troy ounces, to be:

	Minimum	Maximum
Russia	7,115,482	10,128,303
Colombia	700,000	735,000
Borneo	175,000	200,000
United States	10,000	12,000
Canada	9,000	10,000
Other Countries	9,000	10,000
Total	8,018,482	11,095,303

A considerable amount of so-called *scrap platinum,* in the form of old and worn platinum articles, is returned to the refineries, and subsequently sold as new metal. Nearly 50,000 troy ozs. were so treated in the United States in 1927. J. M. Hill estimated that the world's production up to June, 1917, totalled about 5,000,000 troy ozs., and he supposed this to be distributed as follows:

Chemical and Physical apparatus	1,000,000
Electrical plant	250,000
Catalyst	500,000
Dental work	1,000,000
Jewellery	1,000,000
Minor uses and hoarded metal	1,250,000

The market value of platinum fluctuates from year to year, but there is a general tendency for it to rise. An agreement amongst the dealers enables them to control outputs, and to maintain prices without individual competition. In 1880, the price of platinum was between 12*s*. 6*d*. and 13*s*. per oz. troy; in 1890, it had risen to about 25*s*.; and in 1900, to about 63*s*.; in 1910, to about 180*s*. The fluctuations are illustrated graphically in Fig. 2. The subsequent average prices, in shillings per troy oz., were:

	1916	1918	1920	1922
Shillings .	200	400	561	410
	1924	1926	1928	
,, .	538	467	335	

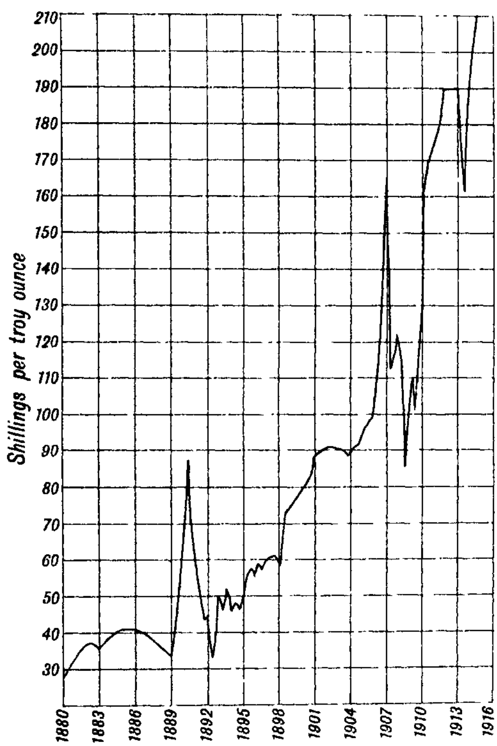

FIG. 2.—The Market Values of Platinum from 1880 to 1915.

The highest price recorded in this period was 770*s*. per oz. troy in January, 1920, and the lowest price recorded was 270*s*. per oz. troy. The subject was discussed by P. A. Wagner, H. B. Kosmann, C. L. Henning, etc.

The price of palladium rose to 800*s*. per oz. troy in 1920, and it then dropped to 350*s*. per oz. troy in 1923. Since then its price has ranged between 180*s*. and 200*s*. per oz. troy. Up to 1914, iridium was sold at about 260*s*. per oz. troy, and the price thereafter steadily rose until it attained 2000*s*. per oz. troy in 1925. The price rapidly dropped to 640*s*. in 1916, and it attained 1800*s*. per oz. troy in 1928. Since then the price has ranged between 1140*s*. and 1200*s*. per oz. troy. Osmium sells at about 240*s*. per oz. troy; rhodium, 225*s*. per oz. troy; and ruthenium, 195*s*. per oz. troy. The price of these three metals is negotiable, being

regulated by the quality and quantity required. According to F. E. Carter, the prices per ounce troy in the United States in 1935 were ruthenium 39.50$; rhodium, 52.50$; palladium, 24.5$; osmium, 50$; iridium, 55$; and platinum, 34$.

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§ 3. The Extraction of Platinum

Platinous sands and gravels are washed in the same way as auriferous sands—**3**. 23, 2—in order to concentrate the metal. The gold is removed from the residue by treatment with mercury. Compact platinum does not amalgamate with mercury in the cold. The residue contains the grains of platinum - alloyed with the other platinum metals, iron, copper, silver, etc.—mixed with grains of osmiridium, titaniferous iron, chromite, spinel, zircon, quartz, and may be some gold amalgam. The washing is sometimes done by hand, sometimes by machines. The process of washing, flotation, and modifications which have been introduced to suit particular cases were discussed by P. von Tunner,[1] C. Schnabel, C. Zerenner, H. Louis, A. von Ernst, A. Laurent, R. P. Rothwell, F. W. Horton, D. T. Day and R. H. Richards, J. Noad, L. Perret, etc.

The extraction of platinum from sulphide ores.—According to P. Wagner,[2] the South African deposits in the Lydenburg, Potgietersrust, and Rustenburg districts are mined by underground shafts. T. K. Prentice and R. Murdoch have described the process used at Onverwacht. The platinum occurs in the metallic state, but by simple gravity concentration the crushed dunite gave a very low grade concentrate, but a satisfactory higher grade concentrate was obtained by the extensive use of traps for metallics, and the treatment of gravity concentrates by amalgamation using activating agents since, unlike gold, platinum does not amalgamate directly when in contact with mercury. The skeleton flow sheet for the dunite ore from the mine, indicated in Fig. 3, will give an idea of the sequence of operations. At the Maandagshoek plant, good results were obtained with the dunite ores by repeating the concentration of the ore along with an acid treatment. Part of the platinum is recovered by flotation. S. C. Smith, T. L. Kapp, and B. W. Holman discussed the subject.

The sulphide ores at Merensky cannot be satisfactorily concentrated by sp. gr. concentration, or by ore flotation, but, by the flotation of the preliminary con-

centrates, 90 per cent. of the platinum metals as well as the nickel and copper can be collected in a concentrate containing 6 to 8 ozs. of platinum metals per ton. With oxidized ores, there is only a 65 to 70 per cent. recovery of the platinum metals, and nearly all the copper and nickel is lost. As recommended by P. Trotzig, the concentrate is therefore smelted to a nickel-iron-copper matte, and this is re-smelted to produce a higher grade matte containing approximately 65 ozs. of platinum metals per ton, and 25·5 per cent. of nickel and 15·5 per cent. of copper. The enriched matte is then roasted, and afterwards leached with sulphuric acid to

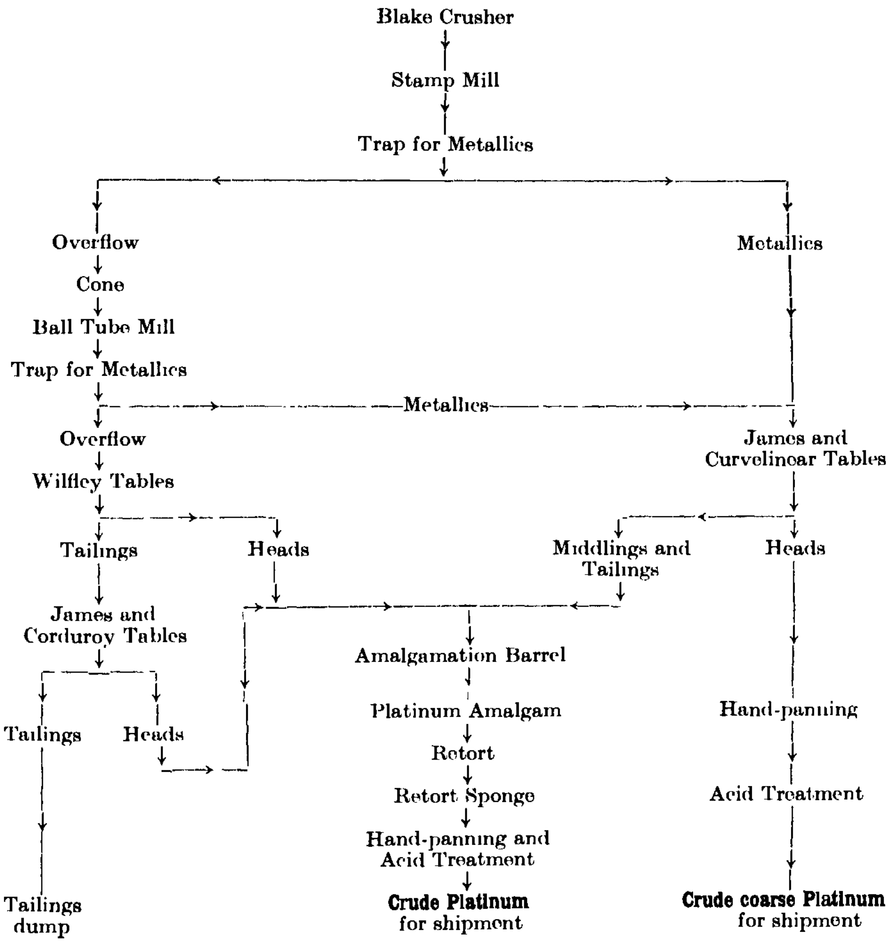

FIG. 3.—Skeleton Flow Sheet for Mined Rock.

dissolve the nickel, copper, and iron. These metals can be recovered by precipitation from the soln. The sludge remaining after the leaching process is smelted to furnish a mass containing 60 per cent. of platinum metals. With about two-thirds sulphide ore, and one-third oxidized ore, this process is said to recover 78 per cent. of the platinum metals; and with sulphide ore alone, 85 per cent. of platinum metals, and 80 per cent. of the nickel and copper in the ore. At Sudbury, where in the extraction of nickel by the Canadian Copper Co., the platinum metals follow the nickel matte, it was found that 56,405 tons of matte produced in 1916 contained 0·10 troy oz. per ton of platinum and 0·15 troy oz. per ton of palladium.

Actually the company recovered 1093 troy ozs. of palladium and platinum, and 257 troy ozs. of other platinum metals—mainly rhodium and iridium.

A. R. Powell and co-workers smelted the ores, concentrates, etc., so as to form a matte and arranged for the matte to contain a free metal of the iron group, to act as collector for the platinum metal; they also added a disintegrating agent—such as sodium sulphate or hydroxide, the carbonate or sulphide of an alkali or alkaline earth. On cooling, the free metal crystallized in coarse crystals from the matte; and on exposure to the air, the matte disintegrated. The product was then crushed, and the free metal crystals separated by a mechanical process such as a magnetic separator or a shaking table, and then treated for the recovery of the platinum metals. K. Wagenmann discussed the extraction of platinum from sulphide ores.

The method employed in recovering platinum from the Sudbury copper-nickel sulphide ores, described by D. McDonald, M. A. Mosher, R. L. Peek, and C. Langer and S. and C. Johnson, depends on whether the crude nickel is purified by electrolysis or by the Mond process. In the former process, the copper-nickel matte is smelted with nitre cake and coke, and after a repetition of the process, the bottom matte, containing the platinum metals along with about 1·5 per cent. of copper and 72 per cent., is broken up, washed with water to remove sodium sulphide, and with dil. acid to remove iron. The washed sulphide is then treated by one of the two following methods:

(i) Roasted with 15 per cent. of sodium chloride between 600° and 1200°; the copper chlorides are leached out; and the soln. led over scrap copper to cement any platinum metals which may pass into soln. The insoluble "green nickel oxide" is then mixed with 20 per cent. of soda ash, and calcined over 1200°; and washed free from sodium salts when "black nickel oxide" with 77·8 per cent. of nickel remains. This is roasted to remove the last traces of sulphur; smelted with coal in an open-hearth furnace, and cast into anodes—about 4 cwt. in weight. The anodes are used for the electrolysis of a soln. of nickel sulphate which is circulated at a greater rate than the migration velocities of the iron and copper, so as to hinder the deposition of iron and copper on the cathode, where nickel is deposited. The cathodes are protected by canvas bags. The anode slimes are dried, melted to metal, cast into anodes which are bagged, and again used in the electrolysis of nickel sulphate in separate cells. The secondary anode slimes so obtained contain about 2 per cent. of platinum metals, and they are concentrated to 40 to 60 per cent. platinum metals by a chemical process.

(ii) Instead of the chloridizing roast, the washed sulphide is finely-ground, roasted, leached with dil. sulphuric acid, and the residual nickel oxide reduced by water-gas to metallic nickel. This is treated with carbon monoxide in Mond's process. The platinum residues which remain after the volatilization of the nickel were found by C. Langer and co-workers to contain Pt, 1·85 per cent.; Pd, 1·91; Au, 0·56; Ir, Rh, and Ru, 0·39; and Ag, 15·42. These residues are smelted with litharge and soda ash to form a lead bullion which is then cupelled, and granulated. The granulations are boiled in conc. sulphuric acid, the palladiferous silver sulphate diluted and precipitated as chloride which is then reduced to metal, cast into anodes, and electrolyzed.

The insoluble material from the sulphuric acid treatment is united with the rich concentrate from the 40 to 60 per cent. concentrate from the electrolytic nickel anode slimes, and digested with aqua regia. The gold is precipitated, cast into anodes and electrolyzed; the palladium is precipitated as palladous diamminochloride; and the platinum as ammonium chloroplatinate.

The platinum concentrates obtained by the above methods require further treatment to isolate the platinum. The dry processes furnish platinum alloyed with more or less iridium, rhodium, etc. None of the dry processes has come into general use. The production of platinum of a high degree of purity from the alloy of the companion metals requires a wet process. According to C. Schnabel,[3]

the electric smelting of the concentrates has not proved satisfactory because platinum absorbs carbon from the carbon electrodes of the furnace as thus loses most of the properties that make platinum of value in the arts.

C. Claus reviewed the older work of F. C. Achard, C. L. Berthollet and B. Pelletier, J. R. Bréant, W. Lewis, A. S. Marggraf, L. B. G. de Morveau, A. Rochon, J. B. L. Romé de l'Isle, T. Scheffer, P. Sobolevsky, L. N. Vauquelin, and W. H. Wollaston. The two following methods illustrate the attempts made near the beginning of the nineteenth century to obtain platinum free from its natural impurities. M. Jeannety recommended repeatedly fusing the ore with a mixture of six parts of arsenic trioxide and two parts of potassium carbonate. The iron and copper are oxidized, and the resulting platinum-arsenic alloy forms a fusible regulus. In 1779, F. C. Achard made "platinum" crucibles from what was virtually a platinum-arsenic alloy. C. Ridolfi recommended melting the ore, previously washed with hydrochloric acid, with 4 times its weight of lead; again heating the granulated mass with an equal weight of sulphur at a white-heat; there is formed under the slag a regulus of a platinum-lead alloy contaminated with sulphur. The sulphur was removed by melting at a white-heat a mixture of the alloy with some more lead. The resulting alloy was said to be malleable.

Dry processes for isolating the metal.—H. St. C. Deville and H. Debray obtained platinum by fusing a mixture of the concentrated ore and lime in the lime-furnace heated by the oxyhydrogen flame, Fig. 6, **3**. 22, 6; and then repeatedly melting the product in a similar furnace, with an oxidizing atmosphere so that the commoner metals are oxidized and absorbed by the lime. The final product is an alloy of platinum, iridium, and rhodium from which platinum can be separated only by the use of a wet process. H. St. C. Deville and H. Debray employed a second process based on the fact that molten lead readily forms an alloy with platinum, but not with osmiridium. Accordingly, a mixture of equal parts of platinum and galena was heated in a small reverberatory furnace provided with a hearth made of calcareous clay, or bone ash. The galena is decomposed by the iron present in the ore, and the liberated lead alloys with the platinum and a lead matte is produced. Litharge is then added, and the whole covered with a fusible glass. The matte is reduced to lead by the litharge, and more platinum-lead alloy is formed, and sulphur dioxide passes off. The osmiridium, which resists attack by the galena, and lead remain near the bottom of the furnace. The slag is skimmed off, and the alloy is removed by a cast-iron ladle. The alloy in the lower part of the furnace is added to the working portion of the next charge so that it is enriched with osmiridium. Finally, the lower portion is poured on a gently sloping surface when the osmiridium remains whilst the platinum-lead alloy runs away. The platinum-lead alloy is heated at a high temp. in a blast, when a large proportion of the lead is oxidized and driven off. The residue is melted as before in the lime furnace by means of the oxy-hydrogen flame. Lead and other volatile elements are volatilized, or the oxides form a slag. The lead-platinum alloy can also be cupelled at a high temp. J. L. Byers studied the effect of platinum on ordinary gold-assay beads. Rhodium and iridium remain with the platinum. G. Matthey, R. Gilchrist, S. F. Schemtschuschny, H. Rusden and J. Henderson described modifications of the process.

J. W. Mellor suggested extracting the platinum metals from dunite and norite ores by blowing the dry, powdered ore through a deep bath of molten lead along with the flue gases previously passed over heated coke. The platinum metals are dissolved by the lead—any forms of platinum not attacked by the molten lead accumulate at the bottom of the bath. When the lead shows signs of "stiffening" by the dissolved metals, it is cupelled, or otherwise treated to recover the platinum. L. D. Hooper, and W. Günther proposed treating the platiniferous ore with carbon monoxide so as to convert the platinum metals into carbonyls, as in the analogous process for nickel. The carbonyls are separated from the ore by volatilization, or by washing with a suitable solvent—like carbon tetrachloride. The carbonyls

of the different platinum metals so produced can be separated by fractional distillation, or differential solubility. A. E. van Arkel, and E. H. Reerink used the carbonyl process for recovering pure platinum.

D. Enzlin and J. A. Eklund passed the powdered ore—dunite, sulphide, or oxidized ore—or concentrate over zinc amalgam in the presence of an activator. The activator is an aq. soln. containing mercuric chloride, zinc chloride, hydrochloric acid and chlorine, with or without the addition of sodium chloride. The zinc amalgam is applied as a coating to an iron or nickel surface. The soln. is mixed with the ore when it is powdered. The amalgam retains the precious metals, and it is afterwards retorted in the usual way. The percentage extraction under favourable conditions is said to approach 75.

Wet processes for isolating the metal.—(1) *Opening up native platinum with aqua regia.*—In most of the wet processes which have tried for isolating platinum, the native metal is first opened up by dissolving it in warm, conc. aqua regia. This was done by L. N. Vauquelin,[4] and W. H. Wollaston, who recommended a preliminary treatment with a magnet to remove iron ore, and cold, dil. aqua regia to extract gold, mercury, and iron. L. Gmelin also recommended a preliminary treatment with conc. hydrochloric acid on a water-bath for several days.

L. N. Vauquelin introduced the dried ore into a retort fitted with a receiver, and added 4 times its weight of aqua regia made from a mixture of 2 parts of hydrochloric acid, of sp. gr. 1·18 with 1 part of fuming nitric acid of sp. gr. 1·48. Another more common mixture is made from 4 vols. of hydrochloric acid, sp. gr. 1·18; 1 vol. of nitric acid, sp. gr. 1·42; and 1 vol. of water. The object of the retort is to confine the poisonous fumes of osmic acid, but W. Lasch added that this precaution is usually unnecessary, although A. Laugier observed that some osmic acid may collect in the acid distillate. To avoid an undue loss of chlorine, J. J. Berzelius recommended covering the platiniferous sand with hydrochloric acid, and adding the nitric acid from time to time. The temp. of the mixture is gradually raised. The process of dissolution is slow since 8 to 10 hrs.' heating in open vessels on a sand-bath with 10–15 times its weight of aqua regia are necessary. E. Barruel recommended acting on the ore first with dil. and then with conc. aqua regia. H. Dullo, and W. C. Heraeus observed that the process of dissolution is hastened if the pressure of the air in the vessel is augmented. H. V. Collet-Descotils, and H. Hess also found that the operation is hastened if the ore be previously fused with 2 to 4 times its weight of zinc. The soln. contains platinum, palladium, gold, iridium, rhodium, ruthenium, base metals, and silver chloride dissolved in the acid liquor; the osmium which is present escapes as volatile tetroxide during the dissolution of the ore. The residue not dissolved by the aqua regia contains the osmiridium with osmium and iridium as the principal constituents with smaller proportions of rhodium, ruthenium, platinum, iron, and copper; the residue also contains sand, chromite, titanite, zircon, etc.

(i) *The precipitation of the platinum by ammonium chloride.*—The platinum metals have now to be recovered from the aqua regia soln. which contains platinum, iridium, rhodium, palladium, iron, copper, and a small proportion of osmium and ruthenium chlorides. H. St. C. Deville and H. Debray evaporated the liquid to dryness, heated the product to redness, when the platinum salts are converted to the metal and the salts of base metals are converted into oxides which can be removed by levigation in water. The residual platinum metals are melted in the oxy-hydrogen furnace. The usual process is to precipitate the platinum as ammonium chloroplatinate, $(NH_4)_2PtCl_6$, from the soln. by the addition of ammonium chloride. In the process devised by W. H. Wollaston, the precipitation of iridium is hindered in the presence of an excess of acid. The ammonium chloroplatinate so obtained was washed, dried, and strongly heated in order to convert it into platinum sponge, which was afterwards compressed and hammered whilst red-hot into bars or rolled into sheets. The first washings from the ammonium chloroplatinate were evaporated to about one-twelfth the original volume to obtain a

mixed iridium and platinum salt; and the second part of the wash-water was evaporated to dryness, heated to redness, and added to a fresh portion of ore. Palladium, rhodium, ruthenium, osmium, and iridium are obtained from the residues which do not dissolve in the aqua regia, and the mother-liquors after precipitation.

C. Claus, W. von Schneider, H. Louis, W. C. Heraeus, and C. Bullman recommend evaporating the aqua regia soln. to dryness, and heating it at say 140° to 150° in order to drive off the nitric acid, and to reduce the iridium tetrachloride to the trichloride. When the residue is dissolved in water or dil. hydrochloric acid, the lower chloride of iridium is not then precipitated with the platinum. An analogous process was used by V. V. Lebedinsky and V. G. Chlopin. A similar remark applies to the palladium and rhodium salts. The liquid is allowed to stand to allow silver chloride and other insoluble matters to settle. Any gold present can be precipitated by ferrous sulphate. If a relatively high proportion of palladium is present, it is advisable to add more ammonium chloride, and nitric acid amounting to 20 to 30 per cent. of the soln. If the liquor is digested on the steam-bath, ammonium chloropalladate may be precipitated along with much of the platinum and iridium in the soln. The presence of nitric acid, however, greatly retards the precipitation of the other precious metals. W. von Schneider tried to prevent the precipitation of iridium and rhodium with the platinum by evaporating the hydrochloric acid soln. nearly to dryness; diluting with water, and making the soln. alkaline with sodium hydroxide free from potassium. The soln. was then mixed with alcohol and boiled, the precipitate dissolved in hydrochloric acid, and the soln. treated with ammonium chloride to furnish ammonium chloroplatinate. The process was discussed by T. Wilm, E. H. Archibald, F. Schulz, W. Halberstadt, K. Seubert, and C. Claus.

W. H. Wollaston sometimes precipitated the palladium as cyanide by adding mercuric cyanide to the aqua regia soln. in which the excess of acid has been neutralized; platinum is precipitated by adding ammonium chloride to the filtrate, whilst the rhodium and the greater part of the iridium remain in the filtrate. To prevent the precipitation of iridium, J. J. Berzelius recommended adding some nitric acid to the soln. H. V. Collet-Descotils, J. Cloud, L. N. Vauquelin, and W. von Schneider discussed the process. F. Wyatt treated the aqua regia soln. with ammonium chloride to precipitate the platinum; then with sodium hydroxide and mercuric cyanide to precipitate the palladium—the rhodium remains in soln. The residue insoluble in aqua regia is heated in a current of air when osmium is converted into volatile osmium tetroxide, and rhodium oxide is deposited in the hotter parts of the tube. The residue is heated with salt in a current of chlorine when sodium chloroiridate is formed which can be dissolved in boiling water.

(ii) *The precipitation of the platinum by other reagents.*—Instead of using ammonium chloride as precipitant for the platinum, the precipitation by potassium chloride was discussed by J. J. Berzelius, C. Bullman, and H. Pirngruber. V. A. Jacquelain tried a mixed soln. of ammonium and potassium chlorides as precipitant. J. W. Döbereiner treated the aqua soln. with lime-water in darkness, but the process does not give a satisfactory separation of iridium and platinum. It was discussed by C. Claus, W. von Schneider, and H. St. C. Deville and H. Debray. After removing most of the platinum as ammonium chloroplatinate, the metals remaining in soln. can be precipitated by iron or zinc, although iridium is reduced very slowly. The washed material is treated with aqua regia (HCl 4 vols., and HNO_3 1 vol.) diluted with 4 vols. of water. Gold and palladium are quickly dissolved, the platinum is dissolved a little more slowly, but very little iridium, rhodium, and ruthenium pass into soln. The platinum can be precipitated from the soln. as ammonium chloroplatinate; the gold, if present, by ferrous sulphate; and the palladium can then be precipitated, as indicated above. These precipitates contain more or less iridium, rhodium, and ruthenium. The remaining metals are

recovered by precipitation with zinc in a soln. from which most of the nitric acid has been removed by evaporation.

L. Duparc said that the process employed in some references for the recovery of all the precious metals in crude platinum involves the following operations:

(i) The treatment of the mineral with aqua regia with the separation of the insoluble osmiridium and sand, etc.

(ii) The precipitation of the platinum as ammonium chloroplatinate and subsequent calcination of the precipitate to produce platinum sponge.

(iii) The separation of iridium as ammonium chloroiridate from the mother-liquor by long standing and calcination of the precipitate to obtain metallic iridium.

(iv) The treatment of the mother-liquors (after removal of the platinum and iridium as stated) with iron, or with zinc, to separate in the metallic state other metals of the platinum group (together with any small quantities of platinum not previously separated) which are deposited as a fine black precipitate called "first blacks."

Drying and roasting of the "blacks" and treatment with dilute sulphuric acid to remove copper and other base metals.

(v) Treatment of the cleaned "blacks" with dilute aqua regia to obtain a solution containing palladium (with traces of platinum, rhodium, and iridium) and an insoluble residue containing rhodium.

(vi) After separating the traces of platinum, rhodium, and iridium from the solution from (v) with ammonium chloride, the palladium is separated by means of metallic iron as a black mass which is purified and the metal sold as palladium sponge.

(vii) The insoluble residue from (v) is fused with barium dioxide, and the fused mass treated with aqua regia to effect solution of the rhodium and iridium. These metals are then precipitated with ammonium chloride and finally converted into metallic sponge.

(viii) The insoluble residue of osmiridium remaining after the first treatment of the ore with acid, is fused with zinc to effect its decomposition. The fused product is treated with aqua regia, and the acid liquor so obtained is submitted to distillation.

(ix) The acid liquor is distilled in the presence of steam whereby osmium distills over as osmic acid, and is collected in water, and the osmium subsequently separated as metal.

(x) The acid liquor retains the iridium and ruthenium which are separated with ammonium chloride, and finally converted into sponge. When the metals are required in a very pure state the commercial metal obtained by processes such as that briefly described above is further purified.

(iii) *The separation of the platinum by electrolysis.*—Platinum can be separated from iridium and rhodium by the electrolysis of an acidic soln. of platinum chloride using a low current density. The Norddeutsche Affinerie [5] used anodes of impure gold containing metals of the platinum group as well as silver, copper, etc.; the cathodes are gold foil; and the electrolyte, a soln. of gold chloride in an excess of hydrochloric acid, or of metallic chlorides which form double salts with gold chloride. Only the gold is deposited at low current densities; platinum is not soluble alone, but it is so when alloyed with gold. The electrolyte is thus enriched in both platinum and palladium. The other metals of the platinum group, along with a little gold, collect as anode slimes; silver forms chloride at the anode and also collects in the anode slime. If the soln. of gold chloride is free from acid, the gaseous chlorine evolved at the anode does not attack the metal, but if an acidic soln. be employed as electrolyte, both gold and platinum are dissolved from the anode. F. Wohlwill assumes that the gold dissolves at the anode only when the electrolyte contains such chlorides as will furnish $AuCl_4$-ions. The platinum is extracted from the electrolyte by precipitation. According to F. Zürn, if the concentrate is made one electrode in a bath of ammonium carbonate or carbamate, and an alternating current is passed through the system, the platinum is converted into carbonates partly soluble and partly insoluble. The carbonate can then be further treated by known processes for the metal. Platinum is also recovered from the anode slimes in the refining of gold by E. Wohlwill's electrolytic process —**3**. 23, 4—and in the refining of silver by B. Mobius' electrolytic process—**3**. 22, 3. A. I. Bochkoff discussed the subject.

(2) *Opening up the native platinum with halogens.*—H. Frasch [6] proposed to extract platinum from sands with a very small proportion of platinum by treating them with chlorine-water which dissolves the metal. K. L. Graham developed a chlorination process for the extraction of platinum from flotation concentrates of

sulphide ores. The dried ore is roasted for 6 hrs. at a dull red-heat to eliminate sulphur, and oxidize thoroughly all the base metals. The product is then mixed with salt and kept at 500° to 600° for about 5 hrs., and at the same time chlorine is passed over the surface of the heated materials so as to convert the metals of the platinum group, copper, and nickel into soluble chlorides. The product is treated with acidified water. The soln. is agitated with powdered limestone to precipitate the copper as carbonate. Only a small proportion of platinum is removed by this process, and it can be recovered from the copper by subsequent smelting and electrolysis. The platinum metals are precipitated as a black powder by agitation with zinc dust. The dried powder is roasted at a red-heat for a few minutes and contains over 70 per cent. of the metals of the platinum group. The residual soln. is treated with sodium hydroxide or bleaching powder. The residue left after the chlorination treatment is treated with cyanide to extract the gold since it is not attacked by the chlorination process owing to the temp. exceeding the dissociation temp. of gold chloride; at the same time, 4 to 5 per cent. of platinum metals are also recovered. About 90 per cent. of the platinum metals and gold are extracted from the concentrate by this treatment. The subject was discussed by T. L. Kapp, and R. A. Cooper and F. W. Watson.

R. Wagner [7] treated the platinum concentrate with a mixture of bromine or hydrobromic acid and nitric acid, and obtained a soln. of the platinum metals which can be treated as in the case of the soln. in aqua regia. E. Bohon treated an amalgam of platinum with nitric acid, and found that silver, mercury, and the base-metals are dissolved whilst platinum and gold are not dissolved. A. Seigle subjected the finely-powdered ore to the action of steam under pressure in the presence of silicic or boric acid and a soln. of chloride of sodium, calcium, or magnesium. If the ore is not sufficiently silicious, silica or boric acid is added to it. For such platinum concentrates, sodium chloride and nitrate are employed, and the nascent chlorine produced is particularly active in converting the metals into a soluble form. If the platinum ore is poor, it should be first treated with a soln. of potassium ferrocyanide through which air is blown, and the product is afterwards treated under pressure in an autoclave. W. Günther exposed the ore to carbonyl chloride under press. so as to convert the platinum into a carbonyl derivative of the chloride, and then leached the ore with a suitable solvent.

The extraction of platinum from residues insoluble in aqua regia.—H. St. C. Deville and H. Debray [8] recommended fusing the residues rich in platinum with enough lead oxide to make an alloy of lead with 25 per cent. of platinum, along with sand, and carbon; with residues with but a small proportion of platinum, in addition to the lead oxide, some glass, lime, and fluorspar were also employed. The resulting alloy was then fused with galena, sand, and an iron silicate sand to isolate the platinum. W. Savelsberg discussed the subject. For F. Wyatt's observations, *vide supra*. R. Gilchrist melted the ore with lead; B. G. Karpoff, with bismuth; and E. Leidié and L. Quennessen, with zinc.

A. Guyard fused the platiniferous residue, insoluble in aqua regia, with 3 times its weight of a mixture of equal parts of sodium hydroxide and nitrate, at a bright red-heat, in a thick wrought-iron crucible, for about an hour. The mixture should be well stirred with an iron spoon during the last 20 minutes, and finally poured into an ingot mould. The product is boiled with water, and the soln. contains sodium osmate. The washed residue is treated with aqua regia, when osmiridium remains undissolved. The soln. contains iron, copper, lead, iridium, rhodium, ruthenium, and platinum. The excess of aqua regia is removed by evaporation, adding some water and hydrochloric acid every now and again to remove the nitrogen oxides. The soln. is then acidified with hydrochloric acid and treated with hydrogen sulphide, at a temp. of 70°, for about 15 hrs. If the mother-liquor is coloured only a pale yellow by the dissolved iridium sulphide, it is filtered, and the precipitate is treated with conc. sulphuric acid which converts the sulphur, and the sulphides of copper and lead into sulphur dioxide and soluble sulphates. The mixture is digested with

water, filtered, and washed until the washings are free from copper and iron. Nitric acid is first added to the precipitated sulphides of the platinum metals, and then hydrochloric acid. The soln. is boiled, and the lead chloride filtered from the cold liquid. The soln. is then treated with ammonium chloride in the usual way.

E. Wichers and co-workers observed that the residue contains mainly rhodium, iridium, ruthenium, and osmiridium, and can be treated by one of the following processes: (i) If rhodium is predominant, the dried residue can be intimately mixed with 2·5 times its weight of sodium chloride, and heated to dull redness in a current of chlorine. This converts rhodium into a soluble sodium rhodium chloride, and some of the iridium is likewise converted into a soluble double chloride, but iridium is less readily attacked than rhodium. (ii) If iridium is predominant, the residue is fused at 600° to 700° with 3 parts of sodium hydroxide and 1 part of sodium dioxide in a silver, nickel, or iron dish. Some iridium forms a basic iridate, but most remains insoluble in water, but soluble in hot, conc. hydrochloric acid. The ruthenium remains in the aq. soln. of the fused mass. Rhodium is not rapidly attacked by the alkali fusion, and that treatment may be alternated with the sodium chloride and chlorine method until all the insoluble material is converted into a soluble form. The mixed soln. of iridium, ruthenium, and osmium can be neutralized with hydrochloric or sulphuric acid and boiled with a little alcohol, and the small amount of metal remaining in soln. can be recovered by the hydrochloric acid-zinc reduction.

When the mixed iridium and rhodium chlorides contain more iridium than rhodium, the soln. is treated with chlorine to oxidize tervalent iridium to the quadrivalent stage, and concentrated by evaporation until over 50 grms. of the two metals are present per litre. Enough ammonium chloride is added to precipitate ammonium chloroiridate, which may also contain rhodium. A large excess of ammonium chloride subsequently interferes with the precipitation of rhodium. The iridium still present in the mother-liquor can be recovered by evaporating the soln. to dryness, to eliminate an excess of acid which would interfere with the subsequent separation of rhodium. The residue is extracted with water, and filtered from the impure ammonium chloroiridate. The filtrate containing not more than 50 grms. of rhodium per litre is boiled and treated with sodium nitrite. This reagent first neutralizes the acid present and reacts with ammonium chloride to form ammonium nitrite, which decomposes in the hot solution. Rhodium and the other platinum metals, as well as certain base metals, are converted to soluble double nitrites, while other base metals, notably iron and tin, are precipitated as hydroxides. Heating is continued and more sodium nitrite added until the colour of the solution becomes yellow or light brown. The precipitate is filtered off and treated for the recovery of the small amounts of platinum metals which it may contain. Ammonium chloride is added to the well-cooled filtrate to precipitate ammonium rhodium nitrite. The granular, white or yellowish salt is separated by filtration, washed with water and dried, or dissolved in hydrochloric acid for further purification. It is not suitable for direct ignition to sponge. Residual metals are recovered from the filtrate by means of hydrogen sulphide.

The recovery of platinum from parted gold and silver.—M. Pettenkofer,[9] L. Opificius, J. W. Klever, and T. Ulke discussed methods for recovering the platinum from parted gold—**3**. 23, 4. M. Pettenkofer recommended the following process for recovering the platinum from the slags produced by melting the parted gold with nitre—or may be with potassium hydrosulphate. The platinum collects in the slag as potassium platinate.

The slag (8 parts) is intimately mixed with galena (2 parts), sodium tartrate (1 part), dry sodium carbonate (4 parts), and powdered glass (2 parts), and added in small portions at a time to a red-hot crucible. The button of lead which is formed collects the platinum metals and gold. The lead alloy is dissolved in hot aqua regia, and the soln. is heated on a sand-bath to drive off the nitric acid. The cold soln. is filtered and the precipitated lead and silver are washed with water. The gold is precipitated by ferrous chloride or sulphate;

and the filtrate is treated with iron to precipitate the platinum. The precipitate is boiled with nitric acid, dissolved in aqua regia, and the platinum precipitated by ammonium chloride in the usual way.

E. Priwoznik used zinc as a collector for the precious metals. Here the gold containing platinum is melted with about 3 times its weight of zinc, and the granulated alloy treated with sulphuric acid to dissolve out the zinc. The washed product is then treated with nitric acid of sp. gr. 1·199 to extract the silver, and again washed. The residual gold-platinum alloy is dissolved in aqua regia, first at ordinary temp., and afterwards warmed. Platinum alone remains undissolved. The soln. containing gold with a small proportion of platinum is mixed with hydrochloric acid, and evaporated in a dish to drive off nitrous fumes. The product is dissolved in water, and the platinum precipitated with ammonium chloride; and the filtrate is treated with ferrous sulphate to precipitate gold.

The separation of platinum and gold has been also discussed by J. P. J. d'Arcet, N. Awerkejeff, W. Bettel, H. Carmichael, M. Chaudet, F. P. Dewey, H. Freudenberg, P. Jannasch and O. von Mayr, H. von Jüptner, G. Kemp, L. G. Kollock, G. Krüss and L. Hoffman, F. Mylius and C. Hüttner, H. Pirngruber, E. Priwoznik, A. D. van Riemsdijk, E. F. Smith and F. Muhr, L. Vanino and L. Seemann, R. Willsättter, and E. Wohlwill.

The recovery of platinum from accumulations from alcoholic washings in potassium determinations by the chloroplatinate process involves distilling off the alcohol, and treating an aq. soln. with some reducing agent—sunlight, hydrogen, sodium formate, sugar, glycerol, zinc, platinum-aluminium couple, etc. The subject was discussed by A. Berthold,[10] A. W. Blair, R. Bottger, C. Brunner, J. Chambers and R. R. Tatlock, W. Dittmar and J. McArthur, E. Duvillier, G. J. Hough, T. Knosel, G. Krause, L. Opificus, L. V. Parisot, E. A. Smith, A. E. Smoll, H. Precht, J. Post, H. C. Weber, H. W. Wiley, E. H. Reerink, J. O. Whiteley and C. Dietz, and W. C. Zeise. The recovery of platinum from other residues was discussed by E. L. Baldeschwieler and L. A. Mikeska, F. Bayer, R. Bottger, A. Stiebel, W. Savelsberg, T. Ulke, C. W. Davis, G. C. Wittstein, H. Wolffram, H. Schwitter, W. Stein, and F. W. Steinmetz.

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§ 4. The Purification of Platinum

Eine Trennung der Platinolemente zu den schwierigsten Aufgaben der Chemie gehört.—H. KAYSER.

As indicated by E. Péchard,[1] the separation of the metals which accompany platinum in platinum ores is *une operation très délicate.* One difficulty is due to the fact that the properties of some of the combinations are very different from those of the individual metals. Thus, iridium and rhodium alone are not attacked by cold, conc. aqua regia, but they dissolve when alloyed with certain proportions of platinum. Conversely, an alloy of platinum and iridium is not attacked by aqua regia when sufficient iridium is present. Again, platinum is not attacked by conc. nitric acid, but it dissolves readily in this acid when it is alloyed with certain proportions of silver (G. von Sickingen), zinc (H. V. Collet-Descotils), or lead (H. St. C. Deville and H. Debray). Many schemes have been devised for the qualitative recognition of the metals present in a given specimen of commercial platinum, or in platinum ores. W. Gerlach, and H. E. Stauss discussed the most sensitive lines for the spectroscopic detection of Si, Fe, Ir, Ni, Os, Pd, Pt, Rh, and Ru in platinum metals. The ore or metal can be " opened up " by dissolution in aqua regia, by dissolution in molten silver or lead and the alloy dissolved in acid ; or the ore can be dissolved in molten sodium dioxide, in a nickel crucible, and the cold mass dissolved in the acid.

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§ 5. Qualitative Recognition of the Platinum Metals

F. Mylius and R. Dietz gave a plan in which the mixed chlorides are boiled in a distilling flask with dil. nitric acid and the distillate collected in a soln. of sodium hydroxide. If osmium is present, the liquid becomes yellow since osmium tetroxide distils over with the steam. The residual liquid is shaken with ether to extract any gold chloride which collects in the ethereal layer. The liquid is then boiled with ammonium acetate and formic acid for several hours in a flask fitted with a reflux condenser, and the black precipitate is washed, dried, and heated to redness in hydrogen. The residue is washed with hydrochloric acid, mixed with sodium chloride, and ignited in chlorine. The product is dissolved in water and treated with ammonium chloride, a precipitate contains the platinum, iridium, and ruthenium, whilst palladium and rhodium remain in soln. (precipitates to left, filtrates to right):

Treat soln. with NH_4Cl

- Add hydroxylamine to the hot aq. soln. of precipitate and then NH_4Cl
  - **Platinum**
  - Evaporate; reduce dry residue in H_2; fuse with $KOH+KNO_3$; extract with water
    - Mix with NaCl; heat in Cl_2; add NH_4Cl; precipitate → **Iridium**
    - Distil filtrate in Cl_2; to volatilize RuO_4 → **Ruthenium**
- Evaporate to dryness with excess NH_4Cl; extract with warm NH_4Cl and cool
  - **Rhodium**
  - **Palladium**

Plans were also given by N. A. Tananaeff and K. A. Dolgoff, S. F. Schemtschuschny and co-workers, I. Wada and co-workers, and W. Graulich. S. C. Ogburg gave the following gravimetric scheme for the separation of the six platinum metals present as chlorides in dil. hydrochloric acid (7 to 8 c.c. HCl per 100 c.c. of soln.):

Add 1 per cent. alcoholic soln. of dimethyl glyoxime in cold; filter

- ↓ **Palladium**, as $Pd(C_4H_7O_2N_2)_2$
- Add excess 2 per cent. alcoholic soln. α-furildioxime; add alcohol 10 per cent. of total volume; boil; and filter
  - ↓ **Platinum**, as $Pt(C_{10}H_7O_4N_2)_2$
  - Concentrate soln. by evaporation; add HCl and $NaClO_3$ to remove excess oximes; add alcoholic soln. KNO_2 until liquid is alkaline; boil; let stand over-night; filter
    - ↓
    - |

Rhodium, as $K_3Rh(NO_2)_6$

Boil to remove nitrogen oxides and alcohol; acidify with HCl; evaporate nearly to dryness; dilute; add alcoholic NaOH; boil; filter

Ruthenium, as $Ru_2O_3.3H_2O$

Evaporate to remove alcohol; acidify with HCl; add zinc; filter

Treat residual Ir and Os metals with a fresh soln. of NaOCl; filter

Reject

Iridium

Acidify with HCl; add zinc dust; filter

Osmium

Reject

For confirmatory tests of the different metals *vide* the analytical reactions of the different metals, and Table I. In the older process for the recognition of the platinum metals, hydrogen sulphide is passed into a hot, acidified soln. of the chlorides until precipitation is complete. The precipitate is digested with warm soln. of yellow ammonium sulphide. Ruthenium, rhodium, platinum, and osmium are not dissolved; platinum, iridium, and gold mixed with arsenic, antimony and tin pass into soln. If these three elements are present, the filtrate is treated

TABLE I.—REACTIONS OF SALTS OF THE PLATINUM METALS

	Ruthenium	Rhodium	Palladium	Osmium	Iridium	Platinum
Colour . . .	Dark brown	Red	Brownish-yellow	Gold-yellow	Dark brown	Pale yellow
H_2S at 18° (1 min.) .	No pp.	No pp.	Brown pp.	No pp.	No. pp.	No pp.
N_2S at 80° (1 min.) .	Bluish-black	Dark brown	Dark brown	Black	Brown turbidity	Dark brown
Amm. sulphide . .	Dark brown pp.; soluble in excess	Dark brown pp.; insoluble in excess	Black pp.; insoluble in excess	Dark brown pp.; insoluble in excess	Brown pp.; soluble in excess	Brown pp.; soluble in excess
Ethyl mercaptan (1 : 100).	Slow brown pp.	Slow yellow pp.	Yellow pp.	No change	Slow decolorization	Pale yellow
Warm NH_4OH . .	Green colour	Slow decolorization	Decolorization	Yellowish-brown pp.		Slow decolorization
Sat. soln. NH_4Cl .	Brown pp.	No pp.	No pp.	Red pp.	Black pp.	Yellow pp.
Alkali lye . . .	Black pp.; insoluble in excess	Yellow pp.; soluble in excess	Yellowish brown; soluble in in excess	Brownish-red pp.	Green soln.; brownish-black pp.	Dark brown pp.
Sat. soln. KCl . .	Violet cryst. pp.	Red cryst. pp.	Red cryst. pp.	Brown cryst. pp.	Brownish-red pp.	Yellow pp.
Soln. KI (1 : 1000) .	Nil	Nil	Dark pp.	Nil	Yellow colour	Slow reddish-brown pp.
Soln. $HgCy_2$ . .	Nil	Nil	White pp.	Nil	Nil	Nil
Soln. KCyS (1 : 1000)	Dark violet	Yellow	Nil	Nil	Decolorization	Intense yellow
Soln. Na_2CO_3 . .	Dark brown	Yellow	Yellowish-brown	Black	Yellow	Nil
Soln. $N_2H_4.HCl$ (1 : 1000)	Yellow	Yellow	Black pp.	Nil	Yellow	Black pp.
Soln. dimethylglyoxime	Nil	Nil	Yellow pp.	Nil	Nil	Nil
HCl soln. cobaltic luteochloride	Nil	Reddish colour	Nil	Nil	Brownish colour	Nil

with hydrochloric acid to precipitate sulphides. The precipitate is fused with a mixture of sodium carbonate and nitrate and washed with water to remove sodium arsenate. Reduce with zinc and hydrochloric acid, and boil with hydrochloric acid to remove tin; boil the residue with nitric and tartaric acids to remove antimony (filtered solids to left, filtrates to right):

Precipitate with H_2S; extract with warm, yellow ammonium sulphide; filter

- Fuse insoluble part with $KOH+KClO_3$; extract with water; filter
  - Ignite in H_2; wash with HNO_3; digest with aqua regia
    - ↓ **Rhodium**
    - Evaporate to dryness; dissolve in water; neutralize with Na_2CO_3; add $HgCy_2$; white precipitate ↓ **Palladium**
  - Neutralize with NHO_3; filter
    - ↓ **Ruthenium**
    - Distil with HNO_3; yellow distillate ↓ **Osmium**
- After the removal of Sb, As, and Sn heat the residue to redness; digest with dil. aqua regia
  - ↓ **Iridium**
  - Evaporate to dryness with excess NH_4Cl; extract with alcohol
    - ↓ **Platinum**
    - ↓ **Gold**

§ 6. Quantitative Determination of the Platinum Metals

The methods available for the determination of the platinum metals when associated with one another in ore, or in alloy, are somewhat complicated. The pioneer work was done by W. H. Wollaston, L. N. Vauquelin, A. Laugier, L. R. von Fellenberg, H. Hess, H. V. Collet-Descotils, F. Döbereiner and F. Weiss, J. Persoz, E. Frémy, C. Ridolfi, F. Wöhler, and J. J. Berzelius. Two general schemes are indicated below. The procedure is necessarily modified according to the number and nature of the metals which have to be isolated. Other schemes have been discussed by H. Arnold, R. Bunsen, A. Classen, C. Claus, W. Crookes, H. St. C. Deville and H. Debray, H. St. C. Deville and J. S. Stas, O. W. Gibbs, L. Wöhler and L. Metz, H. C. Holtz, L. Duparc, V. Rekshinsky, R. Jagnaux, E. V. Koukline, M. C. Lea, E. Leidié, E. Leidié and L. Quennessen, J. W. Mellor, F. Mylius and R. Dietz, O. E. Swjaginzeff, F. Mylius and F. Förster, E. Péchard, L. Quennessen, L. E. Rivot, T. Wilm, and M. Wunder and V. Thüringer.

H. C. Holtz modified the scheme of H. St. C. Deville and co-workers; and the following outline scheme is M. Wunder and V. Thüringer's modification on ore containing iron, copper, gold, rhodium, palladium, iridium, platinum, osmiridium, and sand (solids to left, soln. to right):

Digest with hot aqua regia

- Fuse residue with borax and silver; digest button of metal with nitric acid. There remains undissolved ↓ **Osmiridium**
- Boil to remove HNO_3; add Cl_2-water; evaporate at low temp. to dryness; digest with water; add excess NH_4Cl
  - Ignite and weigh as Pt+Ir; digest with aqua regia
  - Boil with dimethylglyoxime

Iridium

Add NH_4Cl; ignite → Platinum

Gold

Nearly neutralize with NH_3; add dimethylglyoxime

Ignite precipitate → Palladium

Reduce with $Zn + HCl$

Soln. contains → Iron

Digest with dil. $HNO_3(1:1)$

Fuse with $KHSO_4$; extract with conc. HCl

Evaporate with HCl to remove HNO_3, and determine → Copper

Residue contains traces Ir and Pt, and these are separated as above

Add Zn to precipitate → Rhodium

The osmiridium may be dissolved in molten sodium dioxide—as indicated in connection with ruthenium (*q.v.*)—in a nickel crucible, and the cold mass dissolved in hydrochloric acid, and the soln. treated as just indicated for the platinum metals. The ore can be treated with hot aqua regia, and any insoluble residue fused with

Distil the soln. in a current of Cl_2

Boil to remove chlorine; add NH_4Cl, and two-thirds vol. of alcohol

Collect distillate in soda lye; pass H_2S; wash and dry precipitate; heat in oxygen

Ignite; extract with aqua regia

Nearly neutralize with NH_4OH; pass H_2S

Reduce residue in hydrogen → Ruthenium

Collect volatile part in soda lye; reduce with Al → Osmium

Insoluble contains Rh+Ir. Fuse with $KHSO_4$; extract with water and dil. H_2SO_4

Add NH_4Cl to precipitate trace of Pd and Pt. Ignite → Platinum

Digest precipitate with HCl

Evaporate soln. to dryness with HNO_3; ignite; wash out **iron** and **nickel** with HCl; ignite residue for Au+Rh

Add KCl and alcohol to the soln.

Insoluble contains Ir and trace Rh. Dissolve in aqua regia; evaporate to dryness at 120°; dissolve in water; precipitate with Mg; ignite; extract with dil. H_2SO_4, then with dil. aqua regia, and residue → Iridium

Boil with Na_2CO_3; acidify with HCl; dry, and ignite

The precipitate of K_2PdCl_4 contains → Palladium

The soln. contains → Copper

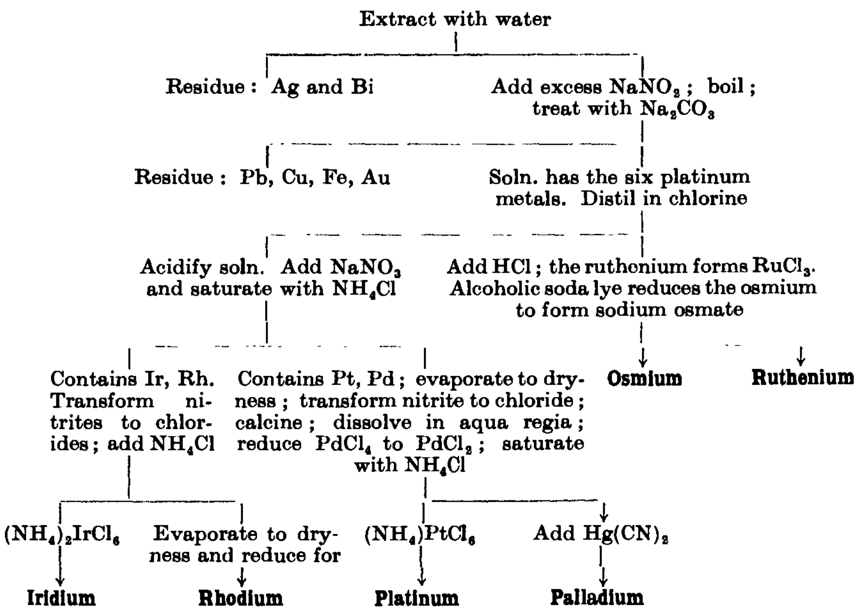
Digest all three residues in aqua regia; the gold dissolves

Insoluble → Rhodium

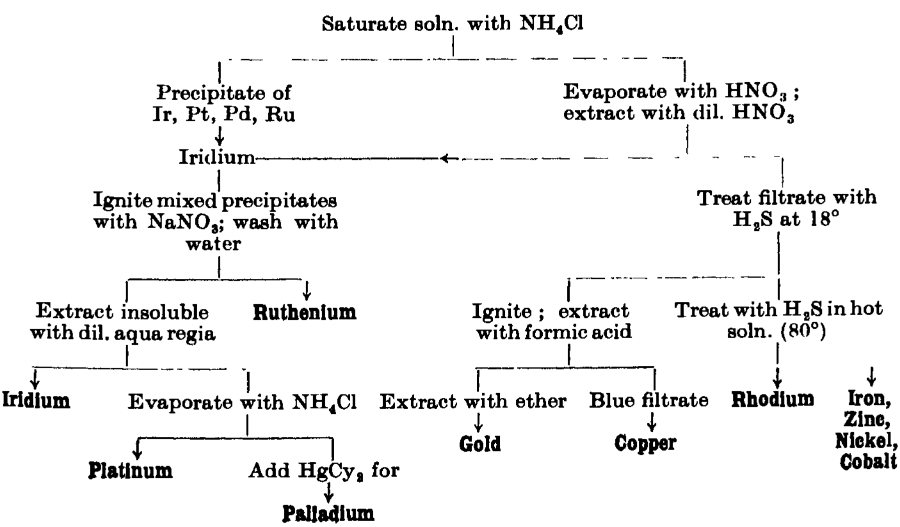
Filtrate contains → Gold

sodium dioxide; the cold cake can be dissolved in hydrochloric acid, and the two soln. mixed. The following metals may be present: ruthenium, rhodium, palladium, osmium, iridium, and platinum, as well as gold, copper, and iron along with nickel derived from the crucible. The scheme recommended by J. W. Mellor, for an ore or alloy containing ruthenium, rhodium, palladium, osmium, iridium, and platinum, as well as gold, iron, and nickel derived from the crucible, is as shown at foot of preceding page (solids on left, soln. on right).

E. Leidié mixed the ore with sodium chloride, and heated the mixture to redness in a current of chlorine:



F. Mylius and A. Mazzucchelli obtained good results in test analyses with the following scheme (precipitation to left, soln. to right):



In order to obtain platinum of a higher degree of purity, J. J. Berzelius[1] neutralized a soln. of platinum in aqua regia by means of lime, or ammonia, saturated the liquid with hydrogen sulphide, and allowed it to stand for a few days in a closed flask. The liquid was filtered from the osmium sulphide, and then treated with potassium chloride. The precipitate was washed with a soln. of potassium chloride until the washings were free from iron chloride. The dry precipitate was heated with twice its weight of potassium carbonate until it began to fuse. The cold product was washed with water, and then with dil. hydrochloric acid. The mixture of platinum and iridium oxide was collected on a filter-paper, washed, and dried. The greater part of the platinum was extracted from the mixture by warm, dil. aqua regia, and the remainder of the platinum was taken up with conc. aqua regia, containing a little sodium chloride to prevent the reduction of the platinic chloride during the evaporation. The soln. was treated with potassium chloride, and the dry precipitate so obtained was gently heated with dry sodium carbonate until the mass blackened and began to fuse. The product containing metallic platinum and the oxides of rhodium and iridium, was washed first with water, and then with dil. hydrochloric acid. The platinum was extracted from the product by aqua regia, and precipitated from the soln. by ammonium chloride.

Following H. St. C. Deville and H. Debray, G. Matthey purified commercial platinum by first melting the crude metal with 6 times its weight of lead, and granulating the alloy. The alloy was then treated with dil. hydrochloric acid which dissolved iron, lead, palladium, and rhodium, leaving behind platinum, iridium, and small quantities of lead, rhodium, and other platinum metals. The residue was boiled with aqua regia, when platinum and lead dissolved, whilst iridium remained behind. The lead was precipitated by sulphuric acid. The filtered liquid was treated with an excess of ammonium and sodium chlorides to precipitate the platinum as ammonium chloroplatinate. When rhodium is present, the precipitate is rose coloured instead of yellow. If rhodium be present, the precipitate is heated with potassium hydrosulphate to form potassium rhodium sulphate whilst the platinum remains as metal. The double salt can be washed out with boiling water. Modifications of the method were employed by H. St. C. Deville and J. S. Stas, E. H. Reerink, and O. J. Broch and co-workers.

E. Wichers and co-workers have pointed out that the repeated precipitation of ammonium chloroplatinate is the most important method of purifying platinum. The salt is relatively insoluble. It may be readily precipitated in a form that is easily filtered and washed, and it may be directly converted to metallic platinum by ignition. Any desired degree of purity may be attained by a sufficient number of reprecipitations. All the platinum metals except rhodium can exist in the quadrivalent state and in this condition form relatively insoluble salts analogous to ammonium chloroplatinate and isomorphous with it. However, because of the usual course of previous separations, osmium and ruthenium are seldom present with platinum except in very small amounts. Palladium is readily reduced from the quadrivalent state to the bivalent state by heating the solution. It is probably true that iridium also is reduced in part, at least, from the quadrivalent state to the trivalent state by heating, especially if the temperature reached 140° to 150° C. The double chlorides of bivalent palladium and trivalent iridium with ammonium chloride are much more soluble than ammonium chloroplatinate and not isomorphous with it. Rhodium, iridium, and palladium display remarkable persistence in contaminating the platinum salt. Platinum containing 0·7 per cent. of rhodium was found to contain 0·2 per cent. after the first precipitation and 0·04 per cent. after the third precipitation. After seven precipitations a minute amount of rhodium could still be detected in the mother-liquor from ammonium chloroplatinate corresponding to about 450 grms. of platinum. Iridium was not detected after the fifth precipitation. This persistent contamination, presumably caused by adsorption, was emphasized by H. St. C. Deville and J. S. Stas. Silver, if

present, may persist for a few precipitations because of the solubility of silver chloride in conc. soln. of chlorides. E. Wichers and co-workers recommend the following procedure:

Crude spongy platinum contained in a porcelain dish with a cover glass to prevent loss by the spray is dissolved in aqua regia—300 to 35 vols. of hydrochloric acid of sp. gr. 1·18, 75 to 100 vols. of water, and 60 to 70 vols. of nitric acid of sp. gr. 1·42. The temp. is raised rather slowly to avoid too vigorous a reaction. In some cases more aqua regia is required for complete solution. The soln. is evaporated fairly rapidly without previous filtration until the temp. reaches 140° to 150° unless the residue becomes pasty before this temp. is attained, in which case the evaporation must be stopped to avoid local overheating. If no large amount of base metal or alkali impurities were present in the sponge, the soln. will be fluid at 150°. A small amount of water is then added, which causes a lively boiling and the evolution of nitrous fumes. In this process any nitrous compounds of platinum are decomposed. L. Duparc and M. N. Tikonowitch state that if the nitrous compounds formed during the treatment with aqua regia are not decomposed, a considerable amount of platinum will escape precipitation with ammonium chloride. More water is added to cool the solution below 100°. After digesting a few minutes some hydrochloric acid is added and the evaporation repeated. This whole process can be repeated three or four times, insuring the elimination of nitrous compounds and presumably promoting the reduction of quadrivalent iridium to the trivalent state. After the last evaporation water only is added and the soln. diluted so as to contain not less than 50 grms. and not more than 100 grms. of platinum in 1 litre. It is set aside to allow settling of insoluble matter and then decanted or filtered from any residue. The residue may contain undissolved iridium or rhodium as well as silver chloride, silica, and other insoluble matter. The soln. is heated nearly to boiling and treated with a 20 per cent. soln. of ammonium chloride, using 55 to 60 grms. of the salt for each 100 grms. of platinum and adding enough in excess so that the whole soln. will contain 3 to 5 per cent. of the salt. A moderate excess of ammonium chloride is desirable to decrease the solubility of the platinum salt but a large excess increases the degree of contamination too greatly. The soln. is cooled rapidly and the salt immediately filtered off and drained by suction. If the soln. is allowed to stand a small amount of salt of much lower purity will separate and thus contaminate the main precipitate. The salt is well drained, returned to the dish and thoroughly mixed with a soln. containing 20 per cent. of ammonium chloride. After draining the salt, this whole process is repeated once more. The filtrates and washings are evaporated to recover most of the residual platinum in a second crop of ammonium chloroplatinate, less pure than the first, and for the recovery of other precious metals by precipitation with zinc. The salt is dried and ignited to sponge.

To avoid the long and tedious sequence of re-precipitations of ammonium chloroplatinate, attempts have been made to abbreviate the process by the collective precipitation of the base metals, and other platinum metals by alkaline reagents. F. Döbereiner and F. Weiss recommended adding milk of lime, or lime water to a soln. of the impure platinum; and F. Mylius and A. Mazzucchelli, a soln. of sodium hydrocarbonate in bromine water—*i.e.* sodium hypobromite. E. Wichers and co-workers also found that good work can be done with alkaline reagents. The reaction is slow in the cold, and to hasten the process, the soln. should be boiled for a few minutes. A reaction between the chloroplatinate and the alkaline soln. tends to make the soln. sufficiently acidic to hinder the complete precipitation of impurities, or to redissolve some of the precipitate. They found that the presence of a bromate retards the hydrolysis of the chloroplatinate. The base metals are readily precipitated in the alkaline soln.; palladium, rhodium, and iridium appear to precipitate very nearly completely; osmium and ruthenium probably precipitate, except for the portion of the ruthenium that is present as nitrosochloride and the osmium and ruthenium that may be oxidized to the tetroxides by the action of the bromate, if the soln. at any time becomes acidic enough to liberate bromine; silver is likely to remain in the soln. as dissolved silver chloride and gold is divided between the precipitate and the soln. However, gold may be eliminated by adding sufficient ferrous sulphate to precipitate it as metal before the addition of sodium hydrocarbonate. The iron from this reagent, of course, is precipitated with the other impurities and may in fact be helpful in collecting small amounts of other precipitated compounds. Some platinum—rarely over 5 per cent.—will appear in the precipitate. E. Wichers and co-workers, and R. Gilchrist and E. Wickers recommend the following procedure:

The soln. of impure platinum in aqua regia is evaporated once or twice to eliminate nitric acid. Enough sodium chloride is added to form sodium chloroplatinate and similar salts of the other metals. The soln. is evaporated and the residue thoroughly dried to remove as much as possible of the hydrochloric acid. The residue is dissolved in water and the soln. diluted so as to contain about 50 grms. of platinum per litre. If gold is thought to be present, ferrous sulphate soln. is added in small portions until no further precipitation of gold occurs. The soln. is decanted from the residue and heated nearly to boiling, after which sodium hydrocarbonate is added in small portions to neutralize most of the remaining hydrochloric acid. When the soln. is nearly neutral, as may be judged by diminishing effervescence, 10 to 12 grms. of sodium bromate for each 100 grms. of platinum are added, only a little being added at first to determine whether the soln. is nearly enough neutral not to decompose the bromate. If bromine is evolved, more sodium hydrocarbonate is added until the addition of a little sodium bromate causes no further evolution of bromine. The remaining sodium bromate is then added and the addition of small portions of sodium hydrocarbonate continued until the soln. just turns sensitive litmus paper blue. The soln. is now brought rapidly to boiling and again tested with litmus paper. If it is acid a little more sodium hydrocarbonate is added and the soln. is then boiled for 3 to 5 minutes. It is finally tested once more, and if not alkaline another small portion of sodium hydrocarbonate is added and the boiling continued for a minute. The soln. is then cooled rapidly in running water. After the precipitate settles, the supernatant soln. is siphoned off and passed through a filter to collect the suspended precipitate. If observations or tests indicate that the reaction has not been successful, the soln. is acidified with hydrochloric acid, evaporated down and the whole process repeated, after adding a little aluminium chloride. The aluminium salt is added so as to produce a precipitate which will collect smaller amounts of precipitated compounds. This is also done when practically pure platinum is being treated. If the separation of impurities appears to have been successful, the soln. is digested with hydrochloric acid to decompose the bromate and the platinum is precipitated with ammonium chloride. The ammonium chloroplatinate precipitated from this soln. will carry down considerable sodium chloride, most of which may be removed by leaching with water after the salt has been ignited to sponge.

E. H. Archibald precipitated the metal from an acid soln. of the platinum as ammonium chloroplatinate; the precipitate was thoroughly washed, dried, and reduced in hydrogen. After removing the ammonium chloride, the platinum-black was boiled with successive portions of conc. hydrochloric acid to dissolve out the iron; and the platinum-black was redissolved. These operations were repeated several times. After three operations, all indications of iridium had disappeared from the spectral lines of the metal. To avoid the difficulty of removing the last traces of nitric acid from a soln. prepared by dissolving the metal in aqua regia, the metal was brought into soln. by making it the anode in an electrolytic cell containing hydrochloric or hydrobromic acid.

B. G. Karpoff and A. N. Fedorova discussed the separation of platinum and iridium; and F. Mylius and F. Förster described the following method of preparing platinum free from iridium. It is based on the conversion of the platinum chloride into sodium chloroplatinate, and purifying this salt by re-crystallization.

Commercially-purified platinum is dissolved in aqua regia, and the soln., freed from nitrogen oxides by repeated evaporation with hydrochloric acid, is mixed with the theoretical amount of purified sodium chloride. The soln. is concentrated to a small bulk, and allowed to cool whilst being continuously stirred; the crystals which separate are freed from mother-liquor by suction, washed with a conc. soln. of sodium chloride, and dissolved in a hot, 1 per cent. soln. of sodium carbonate. The soln. is allowed to cool, when the salt again crystallizes out. It is then dried at 120°, reduced in hydrogen at a low temp., and the resulting platinum sponge is washed for a long time with water, and finally dried and weighed. It is estimated that the product contained 99·99 per cent. of platinum.

P. Bergsöe based a process for preparing platinum free from iridium on the conversion of the platinum in soln. into barium platinocyanide, and purifying the salt by re-crystallization—100 parts of boiling water dissolve 25 to 33 parts of the salt, and 100 parts of cold water, 3·33 parts of salt.

An aqua regia soln. of 40 grms. of platinum containing traces of iridium, mixed with another 0·25 grm. of iridium, was treated with the theoretical proportion of barium hydroxide, and with hydrogen cyanide. The warm mixture was treated with sulphurous acid until it became colourless, and after removing the precipitated barium sulphate,

by filtration of the hot soln., it was allowed to cool to allow the barium platinocyanide to crystallize out. The latter salt is almost insoluble in a soln. of barium chloride. The barium platinocyanide was re-crystallized 3 times from water, and the mother-liquors evaporated to about one-third or one-fourth their vol. and the further separations mixed with the main product. The yield was 75 per cent. of platinum free from iridium. The mother-liquors contained 7·015 grms. of platinum, and 0·281 grm. of iridium. It is believed that this method of purification gives a better product than the sodium chloroplatinate process. Traces of osmium, ruthenium, and rhodium follow the iridium, but palladium, which forms a double cyanide, isomorphous with that of platinum, cannot be removed by this treatment, but it can be expeditiously removed by other processes—*vide supra.*

A number of processes for separating iridium and platinum are based on the reduction of iridium tetrachloride to the trichloride by reducing agents which do not affect the platinum tetrachloride. This prevents the formation of a precipitate of the double salt of iridium when the soln. is treated with ammonium or potassium chloride. Thus, C. Krug reduced the iridium salt with ferric chloride.

The metal was dissolved in aqua regia ; the nitrogen oxides were removed as before ; ammonium chloride was added to the soln. ; the impure ammonium chloroplatinate was dissolved in hot water ; ferrous chloride was added to the boiling soln., until it no longer became paler ; and on cooling iridium-free ammonium chloroplatinate separated out, but the lower chloride of iridium remained in soln. The calcined precipitate was again dissolved in aqua regia as before, and the soln. treated with sodium chloride to precipitate sodium chloroplatinate. The precipitate was dissolved in alcohol, and the soln. filtered from the rhodium, palladium, and ruthenium. The soln. was evaporated to dryness, and the product heated in an atm. of coal gas. The residue was washed with water, dried, and fused on wood charcoal in the oxy-hydrogen flame.

O. W. Gibbs treated the mixed precipitate of ammonium chloroplatinate and chloroiridate with 3 vols. of boiling water, and added a dil. soln. of potassium nitrite until the soln. appeared green, neutralizing the soln. from time to time with potassium carbonate. The iridium then passes into soln. as K_3IrCl_6, whilst the chloroplatinate contaminated with a little iridium remains unchanged. The treatment with potassium nitrite is repeated until the water no longer assumes a green colour. According to A. Joly and E. Leidié, osmium and ruthenium are removed in the form of volatile compounds, and iridium is removed by treatment with lead. A moderately dil. hydrochloric acid soln. of the remaining metals is heated to about 60° and mixed with potassium nitrite. If much platinum is present, potassium chloroplatinate gradually separates as a crystalline precipitate quite free from other metals. After cooling and separation of this salt, the liquid is again heated and further quantities of nitrite are added. Suddenly, and especially if the liquid is stirred, the crystalline double rhodium compound separates, carrying with it lead, bismuth, and tin, and small quantities of copper. If the liquid is allowed to cool, the separation of the rhodium becomes complete, provided that a moderately large quantity of potassium chloride is present. Should iron and copper be present, the addition of the nitrite is continued until the liquid becomes alkaline, and, on boiling, the iron and copper are precipitated, whilst platinum and palladium remain in soln.

M. C. Lea reduced the iridium salt with oxalic acid. The mixed chloroplatinate and chloroiridate were dissolved in just enough hot water for the purpose, and the soln. was treated with crystals of oxalic acid until no more bubbling occurred ; it was boiled for 2 or 3 minutes, half saturated with ammonium chloride, and cooled. The platinum was precipitated as chloroplatinate, and iridium trichloride remained in soln. M. Vèzes separated the platinum by precipitation as potassium platinous oxalato-dinitrite, $K_2[Pt(C_2O_4)(NO_2)_2].H_2O$. According to C. Claus, the mixed ammonium chloroplatinate and chloroiridate can be treated with a little water, and then with an aq. soln. of hydrogen sulphide. Sulphur, and platinum sulphide are precipitated, but iridium sulphide is precipitated only when the hydrogen sulphide is in great excess. The precipitate of platinum sulphide also contains some ammonium chloroplatinate and it yields platinum when calcined. The

mother-liquor also contains some platinum which is recovered by evaporation and treatment with ammonium chloride. A. Bettendorff also employed this process. If the mixed ammonium chloroplatinate and chloroiridate be heated with a little water, and treated with sulphur dioxide, C. Claus found that the iridium salt is reduced and dissolved, whilst the chloroplatinate, being sparingly soluble in sulphurous acid, remains. F. Wöhler and A. Mucklé digested the mixed ammonium chloroplatinate and chloroiridate with potassium cyanide, not in excess, until the residue became pale yellowish-brown, then by recrystallizing the undissolved portion from hot water furnishes ammonium chloroplatinate. C. Claus said that here the potassium cyanide reduces the iridium tetrachloride far more rapidly than is the case with the platinum salt.

According to C. Claus, the mixed soln. of iridium and platinum can be treated with 1 part of sulphuric acid to 3 parts of platinum, and evaporated to dryness. The yellowish-brown mass can be digested with water, filtered, and treated with ammonium chloride to precipitate the platinum. Most of the iridium is transformed into sulphate by this treatment, and only a small proportion of the platinum is affected, the sulphates are not precipitated by the ammonium chloride. C. Birnbaum observed that a mixture of the hydroxides of iridium and platinum can be dissolved in a soln. of potassium sulphite or carbonate, saturated with sulphur dioxide, and boiled with the addition of water until all the sulphur dioxide is expelled, the whole of the iridium is precipitated as sulphite, $Ir(SO_3)_2$; the filtrate contains the platinum which is recovered by evaporation to dryness, and roasting the product.

J. H. Gladstone and A. Tribe treated a soln. of the platinum salt with alkali formate, washed the precipitated metal with conc. nitric acid and then with water. T. Wilm, however, showed that the base metals cannot be removed from metals of the platinum group by reducing agents, since some of the base metals always accompanies the platinum metals—contact action, surface adsorption, or chemical action.

The separation of platinum from *copper* was discussed by W. H. Swanger and E. Wichers; from *gold*, by E. Slatmeanu; from *iridium*, by U. Antony, L. C. A. Barreswil, J. J. Berzelius, C. Claus, W. C. Heraeus, E. Leidié, E. Leidié and L. Quennessen, H. Pirngruber, S. P. Sadtler, W. von Schneider, H. Senn, and E. F. Smith; from *osmium*, by A. Joly and E. Leidié, E. Leidié, E. Leidié and L. Quennessen, and H. Pirngruber; from *palladium*, by C. Brunner, P. Cohn and F. Fleissner, E. Slatineanu, A. Joly and E. Leidié, J. Langness, E. Leidié, E. Leidié, and L. Quennessen, O. Makowka, H. Pirngruber, H. St. C. Deville and J. S. Stas, F. Mylius and F. Forster, and M. Wunder and V. Thuringer; from *rhodium*, by H. St. C. Deville and J. S. Stas, A. Joly and E. Leidié, J. Langness, E. Leidié, E. Leidié and L. Quennessen, E. Wichers, and H. Pirngruber; from *ruthenium*, by H. St. C. Deville and J. S. Stas, A. Joly and E. Leidié, E. Leidié, E. Leidié and L. Quennessen, and H. Pirngruber.

W. Truthe [2] studied the behaviour of the platinum metals towards silver and gold during cupellation at 1100° to 1200°.

Impurities in platinum.—According to C. Claus,[3] platinum free from rhodium and iridium dissolves more easily in aqua regia; if the mother-liquor from the ammonium chloride precipitation is mixed with nitric acid, and heated, it darkens in colour if iridium is present; and if an excess of potassium hydroxide and a few drops of alcohol be added, the mixture blackens if rhodium is present. T. J. Seebeck, and O. L. Erdmann discussed the effect of impurities on the properties of platinum. L. Löwenherz observed 0·02 per cent. of impurities—silver, and rhodium—in commercial "pure" platinum; and J. Weineck, 0·01 per cent. of iridium. F. Mylius and F. Förster observed 2 to 3 per cent. of iridium in commercial platinum; W. P. White always found iridium to be present in commercial platinum; but F. Mylius and R. Dietz observed none in a sample of commercial "pure" platinum. G. C. Wittstein noted some osmium in commercial platinum, but F. Mylius and F. Förster added that platinum prepared by the aqua regia process

is not likely to contain that element ; and in samples of commercial " platinum," and " pure " platinum, they found, respectively :

Pt	Ir	Rh	Pd	Ru	Fe	Cu
96·90	2·56	0·20	Trace	0·02	0·20	— —99·58
99·28	0·32	0·13	—	0·04	0·06	0·07—99·90

H. St. C. Deville and H. Debray analyzed a number of samples and found : platinum, 90·50 to 3·30 per cent. ; iridium, 2·10 to 7·90 per cent. ; and rhodium, 0·30 to 3·30 per cent. O. J. Broch and co-workers found that purified samples contained : 99·890 to 99·892 per cent., platinum ; 0·065 to 0·070, rhodium ; and 0·023 to 0·029, iridium. K. Kraut noted the contamination of platinum with barium ; A. Vogel and co-workers, with chromium ; E. Reichardt, with silicon ; A. Villiers and F. Borg, with zinc ; H. N. Warren, with thallium ; A. Classen, with iron ; and G. C. Hoffmann, and E. Hussak, with copper. W. N. Hartley noted the presence of carbon and phosphorus in a specimen of brittle platinum ; E. Reichardt found silicon in another sample of brittle platinum. T. Wilm said that platinum crucibles become brittle with use if rhodium and palladium are present, because those metals are attacked by the carbon of the coal-gas flame. H. Moser discussed the subject. O. Zvjaginstseff and co-workers did not find dvi-manganese in native platinum.

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§ 7. Some Different Forms of Platinum

Platinum may be prepared in the massive or in the crystalline state—*vide infra*. The metal obtained by the ignition of ammonium chloroplatinate is in the form of a dull grey, soft, spongy powder. To convert this product into malleable platinum the metal must be either fused or welded together. The metal itself fuses at so high a temp. that the manufacture of vessels, or of sheet platinum from ingots cast from the molten metal was impracticable. At first, that is, towards the end of the eighteenth century, attempts were made to reduce the fusibility of the metal by alloying it with a volatile metal, thus F. C. Achard,[1] and M. Jeannety used arsenic; B. Pelletier, phosphorus; and A. von Mussin-Puschkin, mercury. The plates cast from these alloys were heated to drive off the volatile element, and the resulting product hammered together so as to close the pores. The results were not satisfactory.

About 1829, W. H. Wollaston[2] prepared malleable sheets by mixing the finely-powdered metal with a little water, and introducing the "paste" into a brass cylinder so as to avoid inequalities and cavities. The water was pressed out by means of a wooden cylinder, and afterwards the contents of the cylinder were compressed by a powerful lever press. The solid cake was pushed from the cylinder, heated to redness to drive off water and grease, and afterwards heated intensely for 20 minutes in an air-furnace. The red-hot cake is then removed from the furnace and hammered. When the red-hot cake has been sufficiently compressed in this manner, it can, by heating and hammering, like any other ductile metal, be shaped into the required form. The platinum employed should be as free from iridium as possible since the presence of that element is apt to make the platinum brittle. Modifications of the process for preparing **malleable platinum** were discussed by H. Abich, J. J. Berzelius, J. R. Bréant, M. J. Eichfeld, L. W. Gilbert, C. A. Grüel, V. A. Jacquelain, M. Joris, A. Jouglet, M. Leithner, J. von Liebig, C. M. Marx, W. Marshall, J. Pelouze, M. Pettenkofer, B. Scholz, J. S. C. Schweigger, P. Sobolevsky, and W. Spring. The drawing of the metal into wires was discussed by A. C. Becquerel, A. Galffe, H. F. Read, and W. H. Wollaston.

In 1859, H. St. C. Deville and H. Debray[3] described a furnace for melting platinum. It consists of two blocks of lime bound together by an iron casing. In the upper block there is an opening for the oxy-hydrogen blowpipe flame; and in the lower block there is a cavity in which the platinum is melted, and there is also a narrow groove to facilitate the pouring of the molten metal into ingots moulds when the furnace is tilted. It is said that a kilogram of platinum requires for fusion 60 to 100 litres of oxygen—dependent on the purity of the metal. The hydrogen is now usually replaced by coal gas, and improved burners are employed. The subject was discussed by J. B. Dumas, E. Matthey, and H. Violette. Furnaces

were also devised by H. Roessler, and W. E. Newton. C. W. Siemens and A. K. Huntington described a carbon arc crucible furnace for melting platinum, but the presence of carbon is a disadvantage on account of the tendency of the metal to form a carbide. L. Jordan and co-workers, and E. Wichers and L. Jordan recommended melting the metal in a high-frequency, induction furnace filled with a lime hearth; when a magnesia hearth was employed the metal was seriously contaminated with magnesium, and when the metal is melted in a lime crucible, spectroscopic tests indicated the presence of traces of calcium. L. Jordan and co-workers recommended zirconia crucibles; and R. P. Neville, and H. K. Richardson, thoria crucibles. Lime crucibles in the oxyhydrogen flame have the advantage of absorbing some impurities.

The reduction of platinum compounds to the metal.—The platinum salts are easily reduced to the metal, and J. R. Joss [4] observed that the prolonged contact of platinum salts with paper results in a reduction to form **platinum black.** M. C. Lea also noted that solid potassium and ammonium chloroplatinates are partially reduced by a press. of 70,000 atm., and that if characters be marked on bibulous paper soaked in platinic chloride, or ammonium chloroplatinate by a glass rod pressed on the paper, and the paper washed free from soluble salts, characters marked with the rod will appear yellow, or in a few weeks, almost black.

Many salts of platinum decompose to form the metal when heated—*e.g.* platinum sulphide (R. Schneider). Observations were made by G. von Hevesy and T. Somiya, W. F. Bruce, and R. Adams. E. D. Clarke noted the reduction of platinum salts in the oxy-hydrogen flame. W. Müller, and A. Merget noted that the reduction of platinum compounds by hydrogen occurs, in some cases, at ordinary temp., and M. Kling and A. Engels, that the reduction may occur in a current of coal gas. N. Tarugi found that calcium carbide readily furnishes platinum or a calcium-platinum alloy when it is heated with platinum salts.

According to Mrs. Fulhame, W. J. Russell, J. L. Smith, and F. C. Phillips, aq. soln. of platinum salts are reduced by *hydrogen* at ordinary temp. D. Vitali showed that the presence of an arsenic compound favours the reaction, and H. Pellet added that purified hydrogen, freed from all traces of arsenic, does not reduce platinum salts in aq. soln. The slow reduction of platinum salts by *hydriodic acid* was studied by B. Silliman; by *potassium iodide*, by H. Rose, and J. L. Lassaigne; by *sulphur, hydrogen sulphide*, and *alkaline sulphides*, by Mrs. Fulhame; and by *lead or copper sulphide*, by W. Skey. N. W. Fischer found that platinum salts are not reduced by *selenium*, but that they are reduced by *tellurium*. C. A. Tibbals found that platinum salts are reduced by *sodium telluride;* V. Meyer and J. Locher, and W. C. Lossen, by *hydroxylamine* and hydrogen; A. Gutbier and G. Hofmeier, by *hydrazine hydrate;* N. Tarugi, by *hydrazine sulphate* in alkaline soln., but, according to P. Jannasch and O. von Mayr, not in acidic soln.; Mrs. Fulhame, and R. Böttger, by *phosphorus;* Mrs. Fulhame, by *phosphine;* N. W. Fischer, by *arsenic, antimony*, and *bismuth;* T. Polleck, by *sodium dioxide* and a silver salt; D. Vitali, by *silver oxide;* and C. Claus, W. Hempel, W. Skey, and L. Kessler, by *ferrous sulphate*. P. Pascal added that unlike soln. of salts of gold and silver, platinum salts are not reduced in the cold by *ferrous pyrophosphate*. Many other "reducing" salts precipitate metallic platinum—*vide infra*, colloidal platinum.

Mrs. Fulhame, F. W. O. de Coninck, and W. Heintz noted that soln. of platinum salts are reduced by *animal charcoal;* and H. Fresenius and P. H. M. P. Brinton, by over 80 per cent. *alcohol*. The reducing action of *alcohol* was studied by G. Vulpius; of *glycerol*, by F. Bullnheimer; of *ether*, by C. W. G. Kastner; of *formaldehyde*, by N. Awerkijeff, A. Bach, F. Jean and A. Trillat, S. Rothenfusser, and R. E. Liesegang; of *sodium formate*, by J. J. Berzelius, J. W. Döbereiner, C. Claus, E. Duvillier, F. Göbel, B. Corenwinder and G. Contamine, R. Böttger, and B. Sjollema—*vide* A. Sieverts and H. Brüning, hydrochloroplatinic acid; of *acetic acid*, by L. Wöhler; of *alkali acetate*, by R. Brandes; and *oxalic acid*, by

E. Dreyfuss. The reduction does not occur, according to R. Brandes, with *alkali oxalates, citrates, or benzoates.* The reducing action of *potassium ferrous oxalate* was studied by J. M. Eder; of *alkali tartrates*, by R. Phillips; of *organic acids*, by P. Cazeneuve; of *benzene, petroleum,* and *naphtha,* by G. Gore; of *tertiary amines*, by L. Tschugaeff; and of *sugars*, by D. J. Stern and J. Fränkel; and of *glycerol*, by R. Zdrawkowitsch.

The reducing action of *copper* was studied by A. Frumkin and A. Donde, N. W. Fischer—*silver* acts very slowly; of *magnesium*, by Z. Roussin, S. Kern, A. Commaille, R. Böttger, D. Tommasi, K. Seubert and A. Schmidt, A. Schmidt, D. Vitali, F. J. Faktor, I. Nordenskjöld, and N. Tarugi; of *zinc*, by N. W. Fischer, F. Mylius and O. Fromm, and J. Diamant; of *cadmium*, by N. W. Fischer, F. Mylius and O. Fromm; of *mercury*, by E. Sonstadt, C. Barfoed, N. W. Fischer, and F. Bohn; of *aluminium*, by H. W. Wiley, and C. Formenti and M. Levi; N. W. Fischer, *lead*, and *tin*; *molybdenum*, and *tungsten*, by E. F. Smith; *uranium*, by N. W. Fischer, and J. L. C. Zimmermann; *manganese*, by N. W. Fischer; *iron*, by N. W. Fischer; and *cobalt*, by J. Thomsen, and N. W. Fischer.

In 1820, E. Davy [5] prepared platinum in the form of a soft, dull black powder which is called **platinum black,** *noir de platine, Platinmohr* or *Platinschwarz*—B. Geddes discussed the term *Platimoor*. E. Davy said that the platinum black which he prepared soiled any surface on which it was rubbed, and J. von Liebig added that, by pressure, it acquired a white colour, and a metallic lustre. Platinum black is a powerful catalytic agent. E. Davy at first thought it to be a nitrite of platinum, but J. von Liebig showed that platinum black is platinum in a fine state of subdivision. The metal, however, is more or less contaminated by impurities absorbed or adsorbed from the system in which it is prepared. Platinum black was obtained by R. Blondlot by passing an electric current in nitrogen for 3 hrs. between two discs, one of copper and one of platinum, 3 to 4 mm. apart, and heated to bright redness. The black powder on the platinum disc was digested in hot nitric acid to remove the copper, and a residue of platinum black remained. When alloys of platinum with zinc are treated with acids which attack zinc and not platinum, H. V. Collet-Descotils, and J. W. Döbereiner observed that the zinc is dissolved out, and platinum-black remains; J. J. Berzelius used an alloy of platinum and potassium; and L. Gmelin, an alloy of platinum, copper, and zinc with nitric acid. E. K. Rideal, A. A. Pollitt, I. E. Adaduroff and co-workers, I. I. Tschukoff and co-workers, K. von Köppen, and G. Vavon observed that platinum black which has been heated above 300° is less catalytically active. Platinum-black is usually obtained by precipitation from aq. soln. of platinum salts. J. W. Döbereiner, J. H. Kastle and E. Elvove, F. Döbereiner, and J. von Liebig precipitated the platinum with zinc; C. Brunner, with iron; R. Böttger, with magnesium; and F. A. McDermott, with aluminium. W. Hempel used a mixture of ferrous suphate and sodium hydroxide as precipitant; E. Davy, W. C. Zeise, W. Halberstadt, and J. von Liebig used alcohol in alkaline soln.—J. W. Döbereiner observed that sunlight favoured the reduction; W. Halberstadt, ether; A. Sieverts and H. Brüning, R. Willstätter and E. W. Mayer, L. Wöhler, O. Loew, and O. Loew and K. Aso, formaldehyde; A. Gerhardt, formic acid; A. Tribe, potassium formate; F. Göbel, J. W. Döbereiner, L. Mond and co-workers, and A. Gutbier and O. Maisch, sodium formate; J. T. Cooper, sodium tartrate; R. Phillips, ammonium tartrate; R. Böttger, potassium sodium tartrate; M. R. Zdrawkowitch, glycerol and sodium hydroxide; C. Paal, hydrazine hydrate; J. W. Döbereiner, sugar; and A. Sieverts and H. Brüning, magnesium. L. Pigeon, and J. L. Smith employed hydrogen as the reducing agent. C. Luckow obtained platinum black by the electrolysis of a very dil. soln. of platinic chloride. G. R. Levi and R. Haardt discussed the structure of the grains of the powder, and G. von Hevesy and T. Somiya, the preparation of platinum-black with a little lead; the lattice measurements show that the lead is not in solid soln., and measurements of the grain-size, and of the electrolytic polari-

zation were made. O. Loew recommended the following method for preparing platinum black of great catalytic activity:

An aq. soln. (50 to 60 c.c.) of platinic chloride (50 grms.) is mixed with 40 to 45 per cent. of formaldehyde solution (70 c.c.), the mixture cooled well, and then sodium hydroxide (50 grms.) dissolved in water (50 grms.) gradually added; after keeping for 12 hrs. the soln. is filtered. A yellow liquid, from which a small quantity of platinum is deposited on boiling, first passes through the filter, but as soon as most of the salts have been washed out of the residue, the filtrate assumes a deep black colour. The process is interrupted at this stage for several hrs. because the residue soon absorbs oxygen, the temp. rising to 36° to 40°, and the washings then pass through colourless. As soon as oxidation is complete, the residue is washed until completely free from sodium chloride, pressed, and dried over sulphuric acid.

Some kinds of platinum-black deflagrate with a hissing noise when heated—even below redness. According to H. V. Collet-Descotils, that obtained from the alloy of zinc and platinum sometimes detonates like gunpowder—**explosive platinum.** The phenomenon is not the same as that associated with the *fulminating metals*—**3**. 22, 11; and **3**. 23, 14. Explosive platinum was prepared by J. W. Döbereiner, M. Faraday and J. Stodart, W. C. Zeise, R. Bunsen, H. Debray, H. St. C. Deville and H. Debray, J. B. J. D. Boussingault, and T. Wilm. When E. Davy's platinum black is heated, it deflagrates with a hissing noise and a red flame. According to R. Bunsen, and H. Debray, the explosive property is evidence of a peculiar allotropic state of the metal; but T. Strengers, and E. Cohen and T. Strengers showed that in the case of rhodium, and iridium, the phenomenon is due to the union of occluded hydrogen and oxygen.

A film of platinum black may be deposited on platinum foil to be used as electrodes in conductivity measurements, etc. The metal so prepared is sometimes called **platinized platinum.** G. Magnus [6] dipped the platinum in a slurry of water and ammonium chloroplatinate, and after drying, heated to redness. The operation was repeated until a film of the required thickness was obtained. K. Jablczynsky recommended a 0·3 per cent. soln. of platinic chloride, and 3 to 5 c.c. of formic acid made up to 100 c.c. with water. W. Geibel studied the process. The film was obtained by A. Smee, J. C. Poggendorff, and F. Kohlrausch by electrodeposition. O. Lummer and F. Kurlbaum employed as electrolyte about 3 grms. of platinic chloride, 0·02 to 0·03 grm. of lead acetate, and 100 c.c. of water. Two platinum plates are cleaned with chromic acid and lowered into the soln. The current from a 4-volt accumulator is passed for 10 to 15 mins., reversing the direction of the current every half minute. The coating should be "black and velvety" in appearance.

When platinum black is to be employed as a catalytic agent, it is usually deposited as a thin layer on some porous substance. Thus, **platinized asbestos** is prepared by moistening the asbestos with a 10 per cent. soln. of hydrochloroplatinic acid, drying, and igniting the mass. The asbestos was so prepared by R. Hare,[7] and H. N. Warren. Other substances were treated in an analogous manner by W. Boehm, R. Böttger, E. Breslauer, J. F. Duke, J. Klaudy and O. Efrem, W. Majert, M. Neumann, E. Orloff, J. Perl, E. W. von Siemens and J. G. Halske, and C. Winkler. G. P. Thomson, and G. I. Finch and co-workers found that platinized asbestos gives an X-radiogram of asbestos alone; and D. A. Richards added that after the asbestos has been platinized 28 times the X-radiogram of the crystalline platinum appears. The platinum is deposited in cracks in the asbestos, the additional platinizations cause a splitting of the asbestos so that a fresh surface is exposed. The grains of platinum are estimated to be more than 15 A.—or 4 unit cell cubes—and less than 30 A.—or 8 unit cell cubes—in thickness. **Platinized pumice** is obtained by the same process as that employed for platinized asbestos. J. Stenhouse, and M. Figuier likewise prepared **platinized carbon.** E. V. Alexeevsky and I. D. Makaroff soaked the charcoal, previously ignited at 950°, in a soln. of chloroplatinic acid, dried the product at 100°, and reduced it at 120° to 150° with electrolytic hydrogen containing formaldehyde.

A. Piloyan and co-workers, and N. Bakh studied the properties of platinized charcoal; I. E. Adaduroff and K. I. Brodovich, the carriers of the platinum catalyst; and S. Vasileff and A. Frumkin, the poisoning of platinized charcoal as a catalyst. V. N. Morris and L. H. Reyerson, and M. O. Kharmandar and G. D. Dakhnyuk prepared **platinized silica**; and E. V. Alexeevsky and I. D. Makaroff, **platinized clay.**

Metallic platinum can be obtained as a dull grey, soft, and porous mass called **spongy platinum,** *mousse de platine*, or *Platinschwann*. It has the same sp. gr. as platinum, and when rubbed with a hard rod it furnishes flat particles with a metallic lustre. The particles can be welded by heating it to redness and hammering to form sheets and foil. Platinum sponge is obtained by igniting dried ammonium chloroplatinate, preferably in hydrogen. W. H. Wollaston [8] emphasized the need for igniting the chloroplatinate at as low a temp. as possible, to prevent agglomeration, which makes the process a slow one. The preparation of spongy platinum was described by R. Böttger, J. W. Döbereiner, M. Faraday, K. A. Hirschberg, C. W. G. Kastner, J. N. Planiava, and G. Vulpius. Platinum sponge is employed as a catalytic agent, and it becomes less active the higher the temp., and the more prolonged the ignition. R. Feulgen recommended the following process for preparing spongy platinum which does not tend to pass into colloidal soln. during the process of washing before the removal of the chlorides is complete. It is also a very active catalyst.

A soln. of 5 grms. of hydrochloroplatinic acid in 5 c.c. of water is mixed with 7 c.c. of 40 per cent. formaldehyde, and 5 grms. of sodium hydroxide dissolved in 10 c.c. of water are gradually added. The mixture is allowed to remain for half an hour at the ordinary temperature, then heated for 15 mins. at 55° and poured into a half-litre flask half full of water. The flask is agitated violently for a few minutes, which causes the precipitate to settle in coarse particles leaving an almost colourless supernatant liquor. The latter is decanted and the precipitate is washed with water strongly acidified with acetic acid, which again causes the formation of coarse particles which can now be washed as required without showing any tendency to pass into the colloidal state. The metal is finally filtered and dried in a vacuum over sulphuric acid. Great caution must be observed in the subsequent admission of air into the desiccator as the metal readily becomes incandescent owing to absorption of oxygen. Previous to use, it is advisable to grind and wash it once more.

The **plating** of metals, say copper or brass, with platinum has been effected by spreading fine spongy platinum on the metal, then platinum foil, and afterwards rolling at ordinary temp., and at a red-heat. Processes were described by C. Bromeis,[9] M. Labonté and J. Dupuis, and M. Savard. E. Melly was not successful in platinizing metals with thin **platinum films** by using platinum amalgam by the process employed for gilding with gold amalgam, but he did obtain good results by dipping the clean metal in a dil. neutral or alkaline soln. of platinum tetrachloride, and then heating it to 60°; R. Böttger recommended a mixture of 8 parts of sodium chloride with a soln. of 1 part of platinic chloride in 100 parts of water; or a mixture of 1 part of ammonium chloroplatinate with 8 parts of ammonium chloride. Methods were also described by A. P. G. Daumesnil, A. Gawalowsky, J. Stodart, J. H. Johnson, J. A. Paterson, and C. Wilde. For the electrodeposition of platinum, *vide infra*.

A. W. Wright [10] obtained films of platinum on glass by spluttering from an electric discharge in evacuated tubes, and he found the most suitable press. is 1·5 to 1·75 mm. in hydrogen. C. Müller, K. Lauch and W. Ruppert, K. Lauch, F. Rother and K. Lauch, J. Mazur, F. H. Newman, A. W. Gauger, G. I. Finch and co-workers, B. Dessau, C. H. Cartwright, L. Houllevigue, A. Kundt, and J. Patterson also prepared films in an analogous way—*vide infra*. A. Eilert described the preparation of platinum film electrodes. L. Hamburger observed that the film obtained by vaporization in a high vacuum contains ultra-microscopic particles; K. Coper and co-workers found that the layers are not homogeneous.

F. Lüdersdorff prepared **platinum lustres** by pouring a soln. of dry platinic chloride in 95 to 96 per cent. alcohol into 5 times its bulk of oil of lavender. The

platinic chloride dissolves in the oil; and when this mixture is painted on pottery glazes, and fired in a muffle at a dull red-heat, the so-called platinum lustre is produced. Thin films of platinum on porcelain and glass were also obtained by G. T. Beilby, R. Böttger, J. H. Brianchon, L. P. Cailletet, H. Dullo, M. F. L. Ehrlich and C. T. Storck, L. Elsner, A. Salvétat, H. Schwarz, W. von Uljanin, and J. Zuber. C. F. Vasserot prepared **platinum mirrors** and **platinum films** on glass, etc., by mixing 1 part of a sat. soln. of borax in lavender oil with 10 to 15 parts of dry platinic chloride—according to the thickness of the desired film, spreading a uniform coat of the mixture on clean, dry glass, and afterwards fired the coated glass in a muffle at a red-heat. H. Barvir used oil of cloves; R. Böttger, oil of rosemary; L. Elsner, turpentine; and J. Zuber, distilled tar oils. Other recommendations have been made by F. Rother and K. Lauch, H. Barvir, R. Böttger, P. D. Dankoff, J. B. A. Dodé, J. W. Döbereiner, A. Jouglet, O. G. Keiko, L. F. Nilson, A. Salvétat, J. S. C. Schweigger, and H. Schwarz. W. Beetz, and W. C. Röntgen could not prepare perfect films of platinum on glass. S. G. S. Dicker heated the object to be coated with a volatile platinum salt—*e.g.* platinous carbonylchloride. H. Mayer prepared alkali films of atomic thickness on platinum.

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§ 8. Colloidal Platinum

Mrs. Fulhame,[1] in her study of the action of reducing agents on metallic salts in 1794, observed phenomena which would now be interpreted as effects due to the presence of colloidal metals; and the same remark applies to phenomena observed by J. W. Döbereiner, and by A. Schmidt. G. Bredig prepared a **colloidal solution of platinum,** as a **hydrosol,** by spluttering platinum electrodes immersed in ice-cold water—**3**. 23, 10. The process was also employed by G. Bredig and R. Müller von Berneck, A. de Gregorio y Rocasolano, R. Fürth, S. Miyamoto, A. Voet, and C. Ernst. According to E. Müller, the hydrosol is not very stable unless water of the highest degree of purity is employed. M. Kimura observed that when a platinum wire is heated to incandescence, and then plunged into distilled water, the presence of colloidal platinum can be detected by ultra-microscopic examination. H. Kuzel prepared the colloid by bringing the element into a fine state of subdivision by grinding, cathodic spluttering, etc., and then treating it for long periods alternately with dil. acidic soln. and dil. alkaline or neutral soln. under the influence of moderate heat, and violent agitation. After each treatment the material is washed with distilled water or other solvent until it is free from the reagent employed. S. Miyamoto used the silent discharge, E. Jirsa observed that in some cases the colloidal particles are probably oxides.

When a very dil. soln. of a platinum salt, say hydrochloroplatinic acid, is treated with a reducing agent, the platinum which is formed may be in colloidal soln., or a precipitate may be formed, which, when washed with distilled water, is peptized as the associated salts are washed away. K. Regel observed that if potassium chloroplatinate precipitates are treated with magnesium and hydrochloric acid, colloidal platinum is formed. O. Loew, Kalle and Co., H. Schulze, E. C. Auerswald, Y. Shibata and K. Yamasaki, and A. Lottermoser obtained colloidal soln. with formaldehyde as reducing agent in alkaline soln.; K. Shigena, formaldehyde with sodium citrate as peptizer; I. Sano, carbon monoxide. N. Castoro employed acraldehyde as reducing agent; J. Sameshima, coal gas; L. Garbowsky, acetaldehyde, propylaldehyde, valeraldehyde, salicylaldehyde, phenol, pyrogallol, phloroglucinol, resorcinol, hydroxy-acids—salicylic, protocatechuic, gallic, tannic, and quinic acids—vanillin and guaiacol. Benzaldehyde did not give a colloidal

soln. F. Henrich examined the multivalent phenols and photographic developers like eikonogen ; pyrocatechol, in an alkaline alcoholic soln., furnished a deep brown organosol. Kalle and Co. used hydroxylamine as reducing agent ; A. Gutbier, hydrazine hydrate ; A. Gutbier and G. Hofmeier, and G. Hofmeier, hydroxylamine hydrochloride, hydrazine hydrochloride and sulphate, and phenylhydrazine hydrochloride ; A. Skita and W. A. Meyer, hydrogen in the presence of a soln. containing some gum arabic ; Y. Shibata and K. Yamasaki, and J. Donau, carbon monoxide ; L. Wöhler and A. Spengel, an ethereal soln. of phosphorus in the presence of gelatin ; A. Sieverts and E. Peters, sodium hypophosphite, or phosphite ; and J. Meyer, sodium hyposulphite. A. Müller and co-workers obtained colloidal soln. in phosphoric acid.

The stability of the colloidal soln. is greatly enhanced by the presence of protective colloids. R. Zsigmondy, G. Bredig, F. Küspert, A. Gutbier and A. Zweigle, J. Groh, H. Plauson, C. Paal and C. Amberger, S. I. Djatschkowsky, and T. S. Price and J. A. N. Friend used gelatin ; A. Gutbier and co-workers, extract of Irish moss, or extract of quince seeds ; G. Hofmeier, and A. Gutbier and G. Hofmeier, gum arabic ; Kalle and Co., C. Paal, and C. Paal and C. Amberger, sodium protalbinate or lysalbinate ; F. Evers, caoutchouc ; A. H. Erdenbrecher, sugars ; L. Garbowsky, phenol, phloroglucinol, pyrogallol, resorcinol, quinol, catechol, guaiacol, salicylic and gallic acid, protocatechuic acid, tannic acid, quinic acid, acetaldehyde, propaldehyde, valeraldehyde, and salicyaldehyde, but not benzaldehyde ; L. Hugounenq and J. Loiseleur, glycogen ; F. Henrich, eikonogen ; and C. Amberger, lanolin. A. Gutbier and G. Hofmeier, and G. Hofmeier obtained the **hydrogel** by concentrating in vacuo, over sulphuric acid, the colloidal soln. obtained by reducing a soln. of a platinum salt with hydrazine hydrate, in the presence of gum acacia as protective colloid. A. F. Benton made the gel as a shining black substance containing approximately 40 to 50 mols. of water per mol. of platinum by adding a boiling soln. of sodium chloroplatinate—29 grms. of platinum per litre—to a boiling, 5 per cent. of sodium formate, and washing away the electrolyte by decantation ; the second washing, after standing two days, yields the hydrogel.

A series of platinum **organosols** has been prepared by the methods of T. Svedberg —**3**. 23, 10. K. Degen obtained the colloid in alcoholic soln. T. Svedberg found that the colloid is stable in amyl acetate, ethyl acetate, amyl alcohol, *iso*-butyl alcohol, acetone, *n*-propyl alcohol ; but unstable in ethyl ether, chloroform, ethyl alcohol, and methyl alcohol. The stability is not dependent on the dielectric constants of the media. J. Billitzer obtained colloidal soln. in alcohol, and in chloroform ; J. Lindeman and T. Svedberg, in alcohol and ether ; and T. Svedberg, and E. F. Burton, in ethyl malonate. E. C. H. Davies and V. Sivertz studied the rhythmic precipitation of platinum on silica gel. H. P. Walmsley studied the **aerosol** of platinum.

The general properties of the colloidal soln. of platinum were discussed by A. Ivanitzkaja and L. Orlova, W. Pauli and T. Schild, N. P. Peskoff, J. Billitzer, E. F. Burton, H. Freundlich, S. S. Bhatnagar, and E. Jordis. R. Gans and R. Calatroni inferred from the absorption spectrum that the submicroscopic particles of the colloid are, like the corresponding gold and silver amicrons, spherical in form. E. Müller said that the size of the particles is between that of silver and that of gold ; R. Zsigmondy said that the upper limit for the average diameter is $44\mu\mu$; F. Ehrenhaft gave $0{\cdot}58\times10^{-5}$ to $0{\cdot}60\times10^{-5}$ cm. for the mean radius ; E. F. Burton found the diameter is between 2×10^{-5} and 6×10^{-5} cm. ; L. Rolla, $30\mu\mu$; and H. Bechhold studied the passage of the particles through gelatin-filters. S. W. Pennycuick found that the surface of colloidal platinum particles consists of a platinic acid, probably $H_2Pt(OH)_6$. Wo. Ostwald discussed the variation of colour of the colloidal soln. with varying degrees of dispersion. According to E. Müller, the colloidal soln. with very small particles is red, and with particles not so small, the colour is brown. K. A. Hofmann and V. Wölfl observed the ethersol produced with magnesium phenyl bromide has a fine red colour. L. Wöhler and A. Spengel, L. Wöhler, and

B. Delachanal and A. Mermet found that the red colour—**red colloidal platinum**—produced when soln. of platinum salts are treated with stannous chloride is due to the presence of colloidal metallic platinum in a very fine state of subdivision, and that the formation of this in place of the more usual brown colloidal metal is due to the action of stannic chloride and its products of hydrolysis as protective colloids. The red colloid is also formed when the reduction of platinum salts is effected by means of a soln. of phosphorus in ether, if gelatin is added as a protective colloid. The identity of the two red substances has been established by spectroscopic observations. If the colloidal soln. obtained by reduction with stannous chloride is shaken up with ethyl ether or ethyl acetate, the organic solvents take up the red colour, and this is found to be connected with the solubility of stannic chloride in these media, in which it plays the part of protective colloid. When the aq. soln. is diluted with a large volume of water, or when the ethyl acetate soln. is poured into water, a chocolate-brown precipitate is obtained. According to E. A. Schneider, the precipitate has the composition $PtSn_3O_5$, but actually no definite compound is formed because the composition of the precipitate varies considerably with the conditions under which it is produced. It is probable that it is analogous with purple of Cassius, and is a mixture of colloidal platinum and colloidal stannic acid. The properties of the purple of Cassius, and red colloidal platinum are similar.

J. Duclaux found that the osmotic press. of the soln. is less than 2 cm. of water. C. Thomas said that the change to white of the colour of the ultramicroscopic particles marks the beginning of coagulation. P. Lal and P. B. Ganguly observed that the colloid is coagulated by exposure to ultra-violet light. E. Müller studied the polarization, and extinctive coeff. of the colloidal soln.; A. T. Williams, and O. Scarpa, the spectra of colloidal soln. of platinum; E. B. Spear and co-workers, the coagulation of the sol in ultra-violet light; and E. B. Spear and K. D. Kahn, the precipitation of the colloid on metallic surfaces. H. Freundlich observed that the hydrosol of platinum shows anodic convection like arsenic sulphide sol. S. W. Pennycuick studied the cataphoretic velocity. L. Rolla found that the velocity of migration of the colloidal particles in an electric field with a drop of potential of 1 volt per cm. is $24{\cdot}0\times10^{-5}$ cm. per second; T. Svedberg gave for the lower limit $7{\cdot}6\times10^{-3}$ cm. per second; and E. F. Burton, $2{\cdot}3\times10^{-5}$ cm. per second for the speed of colloidal soln. in ethyl malonate. The subject was discussed by A. Einstein, F. Evers, J. J. Bikermann, N. Bach and N. Balaschowa, W. Biltz, and W. R. Whitney and J. C. Blake.

According to L. Liebermann, reddish-brown, colloidal soln. of platinum become dark brown when hydrogen is passed through the liquid. The colloidal soln. of platinum dissolves hydrogen gas roughly in proportion to the concentration. E. C. Auerswald studied the subject. G. Kernot and F. de S. Niquessa found that some protective colloids—*e.g.* gum arabic, dextrin, and albumen—reduce the proportion of gas absorbed, but sucrose has a negligibly small effect. In virtue of the absorbed hydrogen, colloidal platinum favours many reductions catalytically though the activity of the colloid decreases with use, and the chemical work done increases, but not proportionally, with the conc. of the colloidal soln. Thus, C. Paal and A. Schwarz found that acetylene is reduced to ethylene and ethane; and ethylene to ethane. C. Paal and J. Gerum observed that many organic substances such as unsaturated oils are hydrogenized—*e.g.* linseed oil is hardened to a white fat. J. Donau found that a borax bead is coloured reddish-brown by colloidal platinum. J. Eggert found that ferric salts are reduced to the ferrous state; and C. Paal and H. Büttner, that ammonium molybdate is reduced. E. C. Auerswald studied the poisoning of the catalytic activity of platinum hydrosol by mercury.

L. Liebermann observed that the colloidal soln. of platinum contains activated oxygen. C. Paal observed that carbon monoxide is oxidized by oxygen to carbon dioxide in the presence of colloidal platinum; and C. Paal and A. Schwarz, that

hydrogen is oxidized to water. G. Bredig and R. Müller von Berneck studied the catalytic decomposition of hydrogen dioxide by colloidal platinum; the activity diminishes with increasing proportions of protective colloid which may be present. Thus, J. Groh found the effect of increasing the percentage proportion of gelatin on the relative times required to decompose 50 per cent. of hydrogen peroxide:

Gelatin	0·000	0·001	0·010	0·050	0·100
Time for decomposition . .	100	437	460	620	983

According to G. Bredig and K. Ikeda, and T. S. Price and J. A. N. Friend, the activity of the colloid is decreased by hydrogen sulphide or cyanide which are metaphorically said to poison the reaction. C. J. Farmer and F. Parker observed that the activity of the colloid is increased by a short exposure to ultra-violet light, but is decreased with a long exposure until it finally ceases as a black, flocculent precipitate is formed. T. S. Price and J. A. N. Friend observed that the presence of colloidal platinum favours the reaction between hydrogen dioxide and permonosulphuric acid; and J. A. N. Friend, the reaction between hydrogen dioxide and potassium persulphate. G. L. Clark studied the subject.

R. Bärs, R. Fürth, H. P. Walmsley, and L. Hamburger studied the **aerosols** of platinum.

O. Bobertag and co-workers found that the metal in colloidal soln. is flocculated by rapid cooling. G. Bredig's colloidal soln. is flocculated when cooled to $-70°$; and C. J. Farmer and F. Parker noticed that the metal is flocculated by a prolonged exposure to ultra-violet light; and M. Annetts noted that the colloid becomes less stable on exposure to cathode rays. P. B. Ganguly and N. R. Dhar, and E. B. Spear and co-workers studied the subject. E. Müller noted the rapid precipitation of the metal by a few drops of hydrochloric acid. H. Freundlich studied the coagulation of the soln. by electrolytes. A hydrosol, with 0·7 millimol of platinum per litre, is coagulated by soln. of sodium chloride with 2·5 millimol per litre; potassium chloride, 2·2; silver nitrate, 0·22; sulphuric acid, 0·12; sodium hydroxide, 1·30; barium chloride, 0·058; uranyl nitrate, 0·065; lead nitrate, 0·011; barium hydroxide, 0·058; and aluminium sulphate, 0·007. S. W. Pennycuick studied the exchange of ions at the surface of colloidal platinum. W. Biltz found that a trace of ferric, aluminium, cerium, zirconium, or chromium hydroxide precipitates the colloidal platinum from 1 or 2 c.c. of the sol. N. Pappada found that a 4 per cent. soln. of mercuric chloride does not precipitate the colloidal soln. unless it be warmed; soln. of potassium cyanide or hydrocyanic acid change colloidal platinum chemically; there is also a chemical reaction with the halogens—*e.g.* chlorine or iodine; $0{\cdot}1N$-soln. of non-ionized, organic substances—*e.g.* methyl or ethyl alcohol, glucose, and saccharose—coagulate the sol, but N- and more conc. soln. do not do so; 2 c.c. of $0{\cdot}1N$-soln. of hydrochloric, nitric, and sulphuric acids coagulate the sol, likewise also with 1 c.c. of N-CsCl; 1·5 c.c. of N-RbCl—incompletely, and likewise so with N-KCl, N-NaCl, and N-LiCl; coagulation occurs with 3 c.c. of $2N$-KCl; 1 c.c. of $0{\cdot}1N$-$BaCl_2$, $0{\cdot}1N$-$SrCl_2$, and $0{\cdot}1N$-$CaCl_2$; and with 5 drops of $0{\cdot}1N$-$Al_2(SO_4)_3$, and $0{\cdot}1N$-$Cr_2(SO_4)_3$; no coagulation occurred with $0{\cdot}1N$-soln. of CsCl, RbCl, KCl, NaCl, or LiCl, or with the corresponding bromides, iodides, sulphates, or nitrates. The coagulation of the sols was studied by S. W. Pennycuick and R. J. Best, A. Voet, P. C. L. Thorne and co-workers, W. D. Bancroft, Wo. Ostwald, and A. Ivanitzkaja and co-workers. E. B. Spear and K. D. Kahn observed that colloidal soln. of platinum are coagulated by metal plates; and M. Annetts, by cathode rays. The plates are more active if roughened. The order of decreasing activity is: zinc, steel, nickel, tin, and copper. A. de Gregorio y Rocasolano studied the ageing of the sol. Y. Shibata and H. Kaneko studied influence of the sol on the rate of oxidation of pyrogallol.

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§ 9. The Structure of Platinum

R. J. Haüy [1] first suggested that the crystals belong to the cubic system. He said: *la forme de petits cristaux de platine m'a paru être celle du cube;* A. Breithaupt confirmed this with crystals of platinum from Russia; and F. Mohs said that the crystals are hexahedral. G. B. Sowerby found native platinum with a laminated structure. Platinum usually occurs in grains or scales, occasionally in lumps or nuggets weighing up to 21 lbs.—*vide supra.* The structure of these grains was discussed by R. Beck, H. C. H. Carpenter and S. Tamura, B. von Cotta, A. Daubrée, M. Ginsburg, E. Hussak, A. Inostranzeff, B. C. Karpoff, A. Liversidge, S. Meunier, J. Orcel, V. Pöschl, J. W. Retgers, F. Rinne, S. F. Schemtschuschny, and G. H. Stanley and P. A. Wagner. Well-formed crystals are comparatively rare. Cubes or distorted cubes are the most common crystalline forms. P. V. Jeremejeff described some crystals which he said were usually hexahedral, rarely octahedral. No cleavage was observed, but there is some twinning about the (111)-plane. Octahedral forms were also observed by E. Hussak, G. B. Sowerby, and F. Limmer. J. Orcel obtained octahedral and tetrahedral crystals by volatilization. The colour and streak of platinum are whitish steel-grey. F. Mylius and R. Dietz noted that the fracture of platinum is crystalline; native platinum has a hackly fracture. A. Jedele studied the corrosion figures. R. Gans and R. Calatroni discussed the nature of the ultra-microscopic particles of platinum. M. Berek discussed the micro-detection of platinum in ores.

J. J. Ebelmen obtained, by chance, during the fusion of some silicates, octahedral, and cubo-octahedral crystals of platinum; and J. Joly obtained small octahedral or cubo-octahedral crystals by heating platinum in contact with quartz, or topaz. G. T. Beilby observed that the polished metal has a transparent, glass-like skin which may pass into minute scales or granules. A. Guntz and H. Bassett observed that in high temp. electric furnaces, where platinum is near its m.p., the metal may be sublimed to form small crystals 0·0085 to 0·014 mm. in size. These crystals may be cubic or octahedral, or a combination of these forms, or a combination of cubic and tetrahedral forms. G. T. Beilby, and H. Zahn and J. Kramer noted that amorphous layers are converted into the crystalline metal at a definite temp. G. D. Preston studied the twinning of the crystals. G. A. Hulett and H. W. Berger, and H. Moissan observed that small crystals are formed as a dusty sublimate when platinum is heated in the electric furnace; G. P. Thomson and co-workers, the crystalline structure of thin films; and W. Crookes, that platinum sublimed at 1300° furnishes hexagonal plates with a metallic lustre. F. W. Constant observed mosaic crystals.

W. Campbell found that by suitably cooling platinum, a dendritic structure could be developed in the metal. Dendrites, represented by the so-called *platinum tree*, were obtained by G. F. Wach by the action of zinc on a dil. soln. of platinic chloride; and W. Holtz wrapped a zinc-rod (1 mm. thick and 1·5 mm. in width at the bottom, and 3 mm. in width at the top) in paper, and when this was immersed in a soln. of platinic chloride, a platinum tree with many branches was developed. The tree had a metallic lustre and was hard enough to permit of filing.

J. W. Mallet observed that the etching with aqua regia of platinum which has been fused showed up the crystalline structure; and T. L. Phipson observed that the metal etched by aqua regia exhibits octahedral and tetrahedral forms, and

analogous results were obtained by A. Noble, F. E. Carter, F. Limmer, and T. Andrews. F. Bran showed the crystalline structure of the metal which had been exposed to anodic attack in hydrochloric acid. T. Andrews said that the general microstructure of platinum is allotrimorphic in character and derived from a system of interfering cubes and octahedra, the cubic and hexagonal form being frequently noticeable. The size of the larger crystal grains varies from 0·002 inch to 0·04 inch in size, and the smaller crystals range from about 0·0002 inch to about 0·007 inch. J. Orcel, K. Gebhard and H. J. Wiester, O. Feussner, E. Schmid, and F. W. Constant studied the subject. S. Kalischer found that platinum wire which showed no signs of crystallization became distinctly crystalline after being heated to redness. M. Socèze noted that platinum which had been heated for a few days in the vicinity of its m.p., acquired a crystalline structure showing cubic and octahedral forms. L. Holborn and co-workers observed that chemically pure platinum after being heated to 1670° was distinctly crystalline. S. Dembinska found that deposits several $m\mu$ thick show no crystal structure until they have been heated beyond a critical temp., 250° to 300°. O. Feussner showed that platinum does not crystallize on annealing below a certain temp. limit. The curve representing the annealing temp. and grain-size is hyperbolic and concave to the temp. axis so that a relatively small rise of temp. between 800° and 900°, Fig. 4, causes a large increase in the size of the crystals, but a similar rise of temp. between 1200° and 1500° has a very slight effect on the size of thecrystals. Plotting grain-size against the logarithm of the amount of deformation to which the metal has been subjected furnishes a straight line for all temp. The dotted lines in Fig. 4 refer to the effect of temp. on the grain-size. W. Rosenhain also observed a development of the crystalline structure by heating the metal for 4 hrs. in the flame of a bunsen burner. J. F. Daniell, and W. N. Hartley also studied the brittleness of platinum containing carbide, and phosphide. A. F. Noguès heated platinum gauze many hours in a current of hydrogen and observed marked evidence of the formation of cubic and octahedral crystals. J. L. Byers discussed the structure of cupellation beads ; and S. Dembinska, electrodeposited platinum. Z. Jeffries and R. S. Archer observed 450° to be the re-crystallization temp. of platinum. The subject was studied by J. Böhm and P. Feldmann.

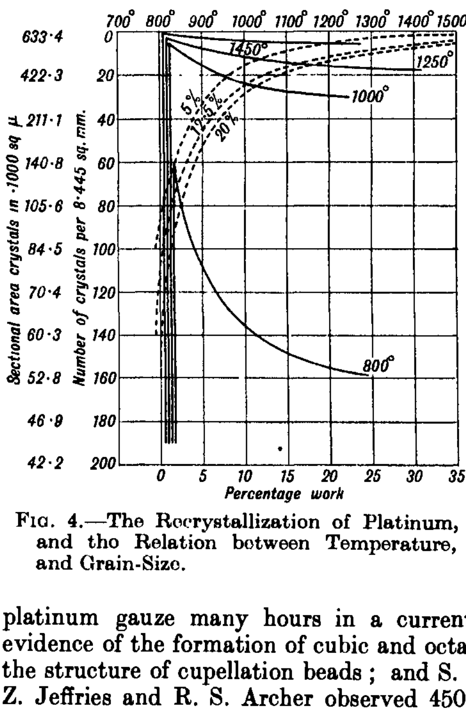

FIG. 4.—The Recrystallization of Platinum, and the Relation between Temperature, and Grain-Size.

According to W. R. Hodgkinson and F. K. S. Lowndes, a platinum wire electrically heated in chlorine acquires a crystalline structure, but not so in bromine vapour. F. Seelheim also obtained lustrous crystals of platinum by passing chlorine over the red-hot metal. L. Troost and P. Hautefeuille observed that if platinum be heated in an inert gas containing a small proportion of chlorine, crystals of platinum appear in the cooler part of the tube. A. E. Törnebohm obtained a similar result by using a mixture of carbon monoxide, air, and chlorine. O. Köttig, and O. L. Erdmann observed that octahedral crystals are formed when platinum is heated at bright redness for some hours in contact with potassium nitrate ; and F. Limmer obtained well-formed crystals by heating the platinum sponge in contact with cupric chloride. H. Moissan obtained crystals of platinum

by the decomposition of platinous chloride at a red-heat; S. Cloez, and L. Pigeon, by the thermal decomposition of platinic chloride; V. A. Jacquelain, and F. Limmer, by the thermal decomposition of potassium chloroplatinate; and W. Spring, by heating the metal with conc. hydrochloric acid in a sealed tube at 150°. H. Behrens found that rolled plates of the metal have a crystalline structure. G. Greenwood found that the cold-worked metal has a fibrous texture resembling that of other face-centred, cubic metals. The (111)-direction is parallel to the drawing force, the texture is somewhat conical, and varies with distance from surface, the interior zones showing the greater fibrous development. J. A. M. van Liempt, H. Mark and K. Weissenberg, A. E. van Arkel, S. Tanaka, R. Vogel, and G. Tammann studied the effect of cold-working. J. A. Ewing and W. Rosenhain observed the development of slip-bands, that is, of lines developed on the surface of metals by plastic strain, and T. and C. R. Andrews showed that when platinum has been subjected to a stress, many of the individual large crystal grains forming the mass, under the influence of the strain, develop innumerable fine stress bands or slip-bands indicating crystalline slip.

The area enclosed by the main lines of disruption roughly approximate to the size of the large crystal grains. The distances between the extremely fine lines or slip bands coincide approximately with the size of the minute crystals forming the mass, the finer slip bands indicate that the crystalline slip has taken place along the facets of the smaller crystals. The direction of the main lines of crystalline disruption do not always coincide with the intercrystalline facet junctions of the large crystal grains. The lines of least resistance or greatest crystalline slip develop chiefly at an approximate angle of 45° to the pressure lines, but the line of greatest weakness in the mass structure of the metal is not always at that angle with the line of the disruptive force.

A. W. Hull found that the **X-radiograms** of platinum correspond with a face-centred, cubic lattice with edge a=3·930 A. The subject was discussed by R. W. G. Wyckoff. N. Uspensky and S. Konobejewsky gave a=4·02 A. for cathodically spluttered platinum; W. P. Davey, and G. Greenwood, gave a=3·912 A.; and T. Barth and G. Lunde, a=3·903 A. H. Kahler found spluttered and ordinary metal have identical lattices. A. E. von Arkel, G. Bredig and R. Allolio, V. I. Iveronova, G. R. Levi and R. Haardt, K. Matukawa and K. Shinohara, G. Natta, E. A. Owen and E. L. Yates, and G. P. Thomson and co-workers studied the subject. G. Bredig and R. Allolio gave a=3·944 A. for the metal, and 3·908 A. for platinum black charged with hydrogen. A. Osawa found that the lattice expands 2·4, 2·9, and 2·8 per cent. when the metal is saturated with carbon monoxide, oxygen, and hydrogen respectively. A. W. Hull, and W. P. Davey calculated that the platinum atoms of the lattice are 2·780 A. apart. F. M. Jäger and J. E. Zanstra observed evidences of dynamic allotropism by observing the change in the X-ray spectrum on a rising temp. R. Salvia found that the lattice dimensions do not permit of the entry of helium atoms. G. I. Finch and co-workers studied the structure of thin films; E. A. Owen and E. L. Yates, the distortion of the lattice by occluded gas; and J. A. M. van Liempt, the heat of loosening of the space-lattice. L. H. Reyerson and co-workers observed X-radiogram patterns on platinum deposited on silica gel.

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§ 10. The Mechanical Properties of Platinum

The **specific gravity** of platinum was reported by A. F. de Fourcroy[1] to be 21·06; and 20·85 for feebly-hammered platinum, and 20·98 for the strongly

hammered metal; P. Musschenbroeck gave 27, M. H. Klaproth, 21·74; M. Chabaneau, 24·0, and J. Cloud, 23·5—all three values are too high; P. Berthier also gave some high values along with 21·47 and 21·53; J. J. Berzelius gave 21·45; M. J. Brisson gave 19·5 for the metal which has been fused; 20·3 for the hammered metal, and 21·0 for the wire; M. Faraday and J. Stodart gave 21·3 for the sp. gr.; D. Prechtl, 17·7 for the fused metal; W. H. Wollaston gave 21·16 for wire, 21·25 for malleable platinum, and 21·4 for the wire drawn from the same metal; B. Scholz gave 21·345; P. T. Meissner, 21·359; C. von Sickingen, 21·061; R. F. Marchand, 21·2668 to 21·3092 at 0°; C. Schumacher, 21·1878 to 20·212; C. Barus, 21·31; R. Hare gave 21·16 to 21·31 for the hammered metal. O. J. Broch said that the mean value of the earlier determinations is 21·49. Collections of data were made by R. F. Marchand, R. Böttger, and F. W. Clarke, and observations on the subject were made by G. Osann. H. St. C. Deville and H. Debray gave 21·15 for purified metal not hardened; and the highest value for the purified metal was 21·504 at 17·8°/17·6°. The lower values were attributed to the presence of sealed pores. W. A. Tilden gave 21·323 at 18°/18°; T. W. Richards, 21·31 at 20°; P. W. Bridgman, 21·34 at 20°; W. Schlett, 21·1296 to 21·4802; G. Wertheim, 20·513 to 20·518 at 10° to 15°; J. Y. Buchanan, 21·5; E. Grüneisen, 21·39 to 21·44; T. W. Richards, 21·31; W. Gaede, 21·407; O. J. Broch and co-workers obtained 21·463 for purified strongly hammered metal; and for the best representative value for a number of samples, they gave 21·49 at 0°/4°; F. Mylius and R. Dietz gave 21·4 for the purified metal. A. W. Hull, and W. P. Davey gave 21·23 for the sp. gr. calculated from the X-radiogram data; and W. P. Davey, 21·51.

G. W. A. Kahlbaum and E. Sturm obtained 21·4316 to 21·4327 at 20°/4° for annealed wire, and 21·4152 to 21·4133 for cold-drawn wire; and G. W. A. Kahlbaum, 21·4 at 20°/20° for the rolled or wire-drawn metal, and 21·1 to 21·3 for the compressed metal. The change in sp. gr. with mechanical work was further discussed by W. Schlett, and F. C. A. H. Lantsberry. T. M. Lowry and R. G. Parker gave 21·3351 for the sp. gr. of the massive metal, and 21·3705 for the filings. G. W. A. Kahlbaum and E. Sturm obtained 21·3985 to 21·4312 for the purified metal, 21·4112, at 20°/4°, after torsion, and 2·4284 after annealing. G. Wertheim gave for the hammered metal subjected to a tensile stress before elongation 21·166 to 21·275, and after cracking, 20·987; and with another sample, 20·753 to 21·207 before elongation, and 21·029 after cracking—all at 12° to 13°—*vide infra*, elastic modulus. J. A. Groshans studied the density relations of the different elements. A. Sayno discussed some relations between the sp. gr., at. wt., m.p., and torsion modulus. G. Quincke gave 18·915 for the sp. gr. of the molten metal.

T. Thomson gave 21·47 for the sp. gr. of spongy platinum; G. Rose, 16·6340; L. Playfair and J. P. Joule, 21·169 to 21·243; E. H. Archibald, 21·16 at 24°/4°; A. W. Warrington gave 21·45 at 0°, and added, $v=v_0(1+0{\cdot}0000266\theta)$. B. Scholz gave 17·894 for the sp. gr. of platinum black; J. von Liebig, 15·80 to 17·572; and G. Rose, gave 20·7732 to 20·9815; and L. Playfair and J. P. Joule, 17·766, but T. Sexl observed that sub-microscopic particles do not have a much lower density than massive platinum. C. Benedicks gave $1{\cdot}37\times10^{-8}$ cm. for the atomic radius; V. M. Goldschmidt, 1·380 A. W. Biltz and K. Meisel, W. Hulme-Rothery, E. H. Westling, J. C. Slater, M. L. Huggins, and G. Hägg discussed the packing density; and G. Destriau, the atomic volume in the solid and liquid states.

H. St. C. Deville and L. Troost [2] discussed the **porosity** of platinum. H. St. C. Deville and H. Debray [3] said that platinum is nearly as hard as copper, and it is readily polished; and W. H. Wollaston observed that in compact masses, platinum is harder than copper, and softer than iron. T. Turner found the **hardness** of platinum on Mohs' scale to be 4 to 5; and J. R. Rydberg, 4 to 4·5. S. Bottone observed the relative hardness of platinum to be 0·1107 when that of copper is 0·1360; and F. C. Calvert and R. Johnson gave iron, 1000; lead, 16; and platinum, 375. C. A. Edwards gave 44 for Brinell's hardness; and F. E. Carter

gave for cast, hard, and annealed platinum, respectively, 50, 97, and 47 ; and for the scleroscopic hardness of hard and annealed platinum, respectively, 21, and 7. Observations were made by P. Rehbinder, C. Johnson, and A. T. Grigorieff. O. J. Broch and co-workers found that a wire supported at its two ends soon acquires a permanent sag. G. T. Beilby observed that the metal is readily hardened and softened. G. Tammann and co-workers studied the effect of cold work on the hardness.

W. H. Wollaston [4] remarked on the high tenacity of platinum wires and found that the metal is very ductile, for it can be drawn out into very thin wires—alone the metal can be drawn to a thickness of $\frac{1}{1940}$th inch ; and when enclosed in silver which is afterwards removed by acid, it can be drawn to $\frac{1}{5000}$th inch, or even to $\frac{1}{30000}$th inch, but in the latter case, the wire is not coherent in long pieces. G. A. B. Klingenstein also observed that the metal can be beaten out into thin laminæ, like gold-leaf. W. H. Wollaston found that the presence of a small proportion of iridium makes the metal harder, and less ductile ; and W. N. Hartley, that the presence of carbide and phosphide makes the metal brittle. K. Karmarsch found that the toughness of platinum lies between that of gold and that of copper ; and A. Baudrimont made a similar observation, and added that the **tensile strength** of a wire 0·410 mm. in diameter was 22·625 grms. per sq. mm. at 0° ; 19·284 at 100° ; and 17·277 at 200°. D. H. Ingall gave 14·27 tons or 32,000 lbs. per sq. in. at 15°. W. Geibel found a wire 1 mm. in diameter broke with a load of 24 kgrms. E. Steinmann studied the effect of annealing—*vide infra*, platinum-iridium alloys. F. E. Carter gave for 0·5 mm. wire, for hard and annealed platinum, respectively, 34 and 15 kgrms. per sq. mm., and percentage elongations in 2 inches, respectively 0·8 and 32. A. Gaiffe noted how dust on the wires during the drawing may interfere with their tenacity. According to P. Phillips, the tenacity, with slow elongation under the action of a constant load, can be represented by $x=a+b \log t$, where t is the time, and a and b are constants. With a load of 500 kgrms. per sq. cm., the value of b is zero, and with increasing loads, the value of b increases. The time t indicates how long the load is acting before elongation begins :

Load .	500	654	771	854	952	1050	1247	1455	1560
$b \times 10^4$.	0	1·525	2·265	3·22	5·39	6·73	26·40	138·0	Fracture

The results are plotted in Fig. 5 with the corresponding values for copper, silver, and gold. The wires were 0·0506 cm. diameter, and were annealed 5 mins. by a current of 8·5 ampères. F. A. and C. L. Lindemann found at the absolute temp. 20·4°, 81°, and 290° K., that the tensile strengths of platinum were, respectively, 8600, 7251, and 5080 kgrms. per sq. cm. F. E. Carter gave for hard and annealed platinum, respectively 17,000 and 15,200 kgrms. per sq. mm. Observations were made by A. G. Grigorieff, and S. Erk. E. M. Wise and J. T. Eash found that purified platinum reduced 50 per cent. by cold work had an ultimate tensile strength of 36,000 lbs. per sq. in., proportional limit 20,700 lbs. per sq. in., elongation 2·5 per cent. in 2 ins., and reduction in area 95 per cent. ; when fully annealed at 1100°, the ultimate tensile strength was 20,700 lbs. per sq. in., elongation, 30 per cent. in 2 ins., and reduction in area 93 per cent. The addition of alloying elements in moderate amounts markedly increased the strength, and annealing temp., without detriment to the ductility.

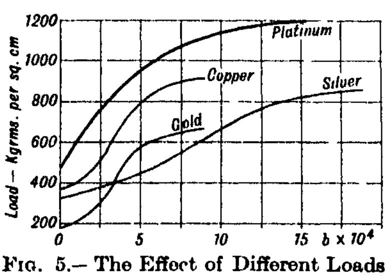

FIG. 5.—The Effect of Different Loads on the Tensile Strength of Platinum.

F. Kohlrausch gave 17,020 kgrms. per sq. mm. for the **elastic modulus** or *Young's modulus* of platinum ; E. Edlund gave 16,275 kgrms. per sq. mm. ; C. Schaefer, 16,029 kgrms. per sq. mm. ; and E. Grüneisen obtained two samples,

respectively, 17,021, and 17,080 kgrms. per sq. mm. G. Wertheim found the elastic moduli, E kgrms. per sq. mm., of drawn and annealed wires to be:

	Thin wires		Medium wires		Thick wires	
	Drawn	Annealed	Drawn	Annealed	Drawn	Annealed
E . . .	16,052	14,332	17,159	15,483	15,986	16,748
Sp. gr. . .	21·166	20·753	21·275	21·083	21·207	20·987

For drawn platinum wire, N. Katzenelsohn gave 17,187 kgrms. per sq. mm.; K. F. Slotte, 15,989; G. Wertheim, 17,044; H. Tomlinson, 16,225; and A. Winkelmann, 16,926 kgrms. per sq. mm.; and for annealed platinum wire, G. Wertheim gave 15,518, and G. S. Meyer, 16,020 kgrms. per sq. mm. K. R. Koch and C. Dannecker's results, Fig. 6, show that the elastic modulus is nearly constant as the temp. rises to 400°, after which it falls. W. Sutherland found the extreme values which have been reported were 14,370 and 17,770—mean 16,000. Observations were made by A. T. Kupffer, A. G. Grigorieff, M. Cantone, M. Ascoli, L. P. Sieg, O. Feussner, and N. Gesehus. A. Wassmuth found the temp. coeff. of the elasticity coeff. is $0{\cdot}0_4978$. C. Schaefer gave 0·732 for the temp. coeff. of the elastic modulus in percentages for 100° difference of temp. between 0° and —186°. G. Wertheim gave for the elastic modulus of annealed platinum 15,518 kgrms. per sq. mm. at 10° to 15°; 14,178 kgrms. per sq. mm. at 100°; and 12,964 kgrms. per sq. mm. at 200°; and for the unannealed metal, 15,647 kgrms. per sq. mm. at 10°, and 16,224 kgrms. per sq. mm. at —15°. W. Widder gave for the modulus of elasticity, $E = E_{20}\{1 - 0{\cdot}0005734(\theta - 20)\}$. K. F. Slotte gave:

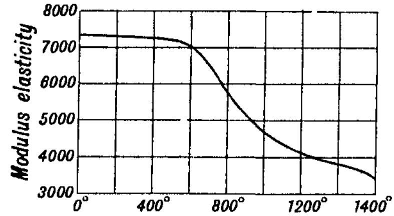

FIG. 6.—The Effect of Temperature on the Elastic Modulus of Platinum.

	10°	20°	30°	50°	70°
E .	16,210	15,989	14,711	13,947	13,759 kgrms. per sq. mm.

H. Tomlinson gave for Young's modulus, 1490×10^6 grms. per sq. cm.; and A. Mallock, 1·27 for the ratio of Young's modulus at —273° and at 0°. P. Lasareff found the elastic limit is proportional to $n^{5/3}$, where n is the number of atoms per c.c. E. Grüneisen gave 1·0014 for the ratio of the adiabatic to the isothermal elastic modulus; and 0·368 to 0·387 for **Poisson's ratio,** *i.e.* the ratio of the lateral contraction to the longitudinal extension; C. Schaefer gave 0·22; F. E. Carter, 0·387; and H. Tomlinson 0·076. G. M. F. Sayre studied the elastic after-effect; and G. Tammann, the effect of cold-work on the physical properties.

C. Schaefer found the **rigidity** or **torsion modulus** to be 6593·6 kgrms. per sq. mm.; E. Grüneisen gave 6220 kgrms. per sq. mm. at 18°; W. Sutherland gave 6500; H. Tomlinson, 6620; F. Horton, 6585; G. Pisati, 6280; A. T. Kupffer, 6370; and B. Gutenberg and H. Schlechtweg gave $6{\cdot}8 \times 10^{22}$ dynes per sq. cm. K. R. Koch and C. Dannecker observed that the effect of temp. on the torsion modulus T kgrms. per sq. mm., and the damping coeff., K, of wires 1·507 mm. in diameter, and 372·0 mm. in length is small, being

	0°	200°	400°	600°	800°	1000°	1200°	1400°	1600°	1700°
T .	7240	7240	7200	6940	5740	4710	4130	3600	3300	2860
K .	1·001	1·001	1·001	1·024	1·108	1·101	1·13	1·17	1·27	1·5

F. E. Carter gave 6·10 dynes per sq. cm. for the rigidity; and H. Tomlinson, $692{\cdot}7 \times 10^6$ grms. per sq. cm. Observations were made by R. H. M. Bosanquet, J. Königsberger, A. G. Grigorieff, K. Iokibe and S. Sakai, and G. Wertheim. P. W. Bridgman observed that the rigidity increases under press. 2·4 per cent. per 10,000 kgrms. per sq. cm.; and that there are no breaks in the curves of shearing stress and pressure. The subject was discussed by L. H. Adams. The elastic

after-effect was found by E. Rehkuh to increase slightly with rise of temp. H. Sieglerschmidt studied the relation between the elastic modulus and the thermal expansion; O. Förster, the relation between the elastic modulus, the sp. ht., and the at. wt.; L. P. Sieg, the relation between the elastic modulus and the m.p.; H. Jeffreys, the relation between the tensile strength and the m.p.; A. H. Stuart, and J. Kleiber, the relation between the elastic constants and the sp. ht.; and A. Sayno between the sp. gr., the at. wt., the m.p., and torsion modulus. W. Sutherland gave $e/E=1-0{\cdot}823\theta/T_m$, where e denotes Young's modulus at $\theta°$, and E, at absolute zero; and T_m is the m.p. of the metal. The relation is imperfect because it gives a finite value for the modulus at the m.p. whereas it ought to give a zero value. Otherwise the observed values are approximately in accord with the expression. A. Jacquerod and H. Mügeli gave for the **bending elasticity** of platinum 19,900 kgrms. per sq. mm. at 0°, and 0·000075 for the temp. coeff. between 0° and 100°. F. E. Carter gave for the **volume elasticity** 24·7 dynes per sq. cm.; and for Ericsen's **ductility** test of hard and annealed platinum, respectively, 7·8 and 12·2 mm. K. Iokibe and S. Sakai gave for the **rigidity** and **logarithmic decrement,** for periods of about 10 seconds:

	27°	191°	369°	604°	743°
Rigidity $\times 10^{-11}$ . . .	6·41	6·33	6·18	5·80	5·04
	26°	191°	385°	604°	690°
Log. decr.	0·0$_3$25	0·0$_3$35	0·0$_3$97	0·0220	0·0500

and for the **viscosity** $n=1{\cdot}75\times10^8$ at 15°. The subject was investigated by T. Kikuta, and G. Subrahmaniam.

T. and C. R. Andrews found that the stress required to compress a platinum cube, of edge 0·30 inch, down to 10 per cent. of its original height, is 12·82 tons per sq. in. E. Grüneisen gave $0{\cdot}04\times10^{-12}$ c.g.s. units for the cubic **compressibility** of platinum, and $0{\cdot}39\times10^{-6}$ to $0{\cdot}40\times10^{-6}$ for the coeff. of cubical compressibility; he found the effect of temp. on the coeff. of cubic compressibility β, to be:

	−189°	16·8°	133°	164°
$\beta\times10^6$	0·374	0·392	0·401	0·404

The compressibility thus increases with rise of temp., whereas the coeff. of thermal expansion decreases with a rise of temp. The results with a few metals are illustrated by the curves, Fig. 7. L. H. Adams gave $0{\cdot}3\times10^{-6}$ to $0{\cdot}37\times10^{-6}$ megabars. P. W. Bridgman gave for wire at 30° $\delta v/v=-10^{-7}(3{\cdot}60-1{\cdot}8\times10^{-5}p)p$, and at 75°, $\delta v/v=-10^{-7}(3{\cdot}64-1{\cdot}8\times10^{-5}p)p$; and for rod at 30°, $\delta v/v=-0{\cdot}0_6305p$, and at 75°, $\delta v/v=0{\cdot}0_6309p$. If β denotes the metal compressibility at 30°, and a, the coeff. of thermal expansion, P. W. Bridgman gave $\beta=0{\cdot}0_6305$ for drawn rod, and $0{\cdot}0_6360$ for drawn wire at 30°; $(d\beta/\beta dp)\times10^{-5}=1{\cdot}00$; and $-(da/adp)\times10^5=0{\cdot}33$. T. W. Richards found that the compressibility represented as the change in vol. which occurs between 100 and 500 atm. press. is $0{\cdot}21\times10^{-6}$ megabars. J. Y. Buchanan gave 0·1835 for the linear compressibility in million vols. per atm. press. B. Zdanoff studied the compressibility coeff. of crystals. E. Wagner deduced values for the effect of press. on the electronic density, and the electrical conductivity.

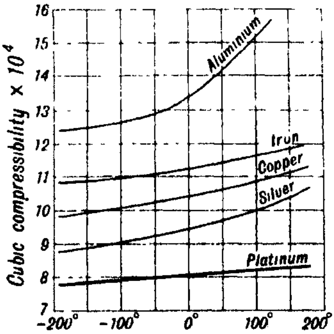

FIG. 7.—The Effect of Temperature on the Compressibility of Platinum.

A. Press, J. P. Andrews, E. Grüneisen, S. Ratnowsky, W. Wen-Po, G. F. Djang, and A. H. Stuart studied the relation between the thermal expansion, at. vol., and compressibility; W. Widder, the m.p.; R. von D. Wegner, and G. A. Tomlinson studied the internal cohesion; and R. Holm and B. Kirschstein, the adhesion.

C. E. Guye and H. Schapper [5] measured the **viscosity** of platinum at different temp. and found that with wires 23 cms. long, and 0·8117 mm. diameter, the damping coeff. *c*, the period of oscillation, *O* seconds, and the second elastic modulus, *N*, were :

	100°	50°	0°	180°	−195°
C	2·976	3·457	4·596	4·276	3·024
O	1·143	1·135	1·133	1·123	1·111
$N\times 10^{-11}$	5·769	—	—	—	6·698

B. Gutenberg and H. Schlechtweg gave $1·7\times 10^8$ c.g.s. units at ordinary temp. C. E. Guye and S. Mintz studied the effect of temp. on the viscosity, and found that in passing from a high to a low temp. the original logarithmic decrements are not obtained. These differences are smaller the higher is the temp. S. Virtel studied the resistance law for the motion of sub-microscopical particles through gases ; and F. Hirata, through viscous liquids. M. Born and O. F. Bollnow calculated the cohesive force of the atoms in the space lattice to be $5·62\times 10^{11}$ dynes per sq. cm.

T. W. Richards [6] calculated for the **internal pressure** 347,000 megabars at 20° ; and this value is exceeded only by tungsten. J. H. Hildebrand and co-workers, and R. H. Mehl studied the cohesive press.

D. V. Gogate and D. S. Kothari [7] gave 1819 for the **surface tension** of platinum at 2000°. G. Quincke calculated the **capillarity** coeff. of hard, drawn platinum to be 3025 grms. ; annealed platinum, 2388 grms. ; and molten platinum, 169·04 mgrms. P. Palladino said that methylene bromide gives a concave meniscus with platinum ; S. L. Bigelow and F. W. Hunter studied the effect of platinum walls on the capillarity of water, and of benzene ; and E. Warburg and T. Ihmori, the effect on the capillarity of water. E. Degen discussed the wetting of platinum by water ; and F. E. Bartell and M. A. Miller, the adhesion of water to the metal.

The **diffusion** of various gases, etc., in platinum was studied by C. Matteucci,[8] and G. Moreau, and the subject is discussed in connection with the chemical properties of the metal. W. Kettembeil, and A. Coehn and W. Kettembeil observed that mercury does not diffuse in platinum, but N. T. M. Wilsmore found that platinum amalgam will make platinum swell. W. C. Roberts-Austen observed that platinum diffuses more rapidly in bismuth than it does in lead. The diffusion coeff. for platinum in lead is 1·69 per sq. cm. per day, at 492°.

O. D. Chwolson [9] gave 2700 metres per second for the **velocity of sound** in platinum ; A. Masson gave 2792·1 metres per second ; and G. Wertheim gave 2684·9 metres per second for drawn wires, and 2733·4 metres per second for annealed wires. J. Kleiber found that the velocity of sound in metals is proportional to the sq. root of the product of the sp. ht. and the linear coeff. of expansion. Relative values were calculated by G. Wertheim on the assumption that the velocity in air is unity :

Thin wires		Medium wires		Thick wires	
Drawn	Annealed	Drawn	Annealed	Drawn	Annealed
8·241	7·832	8·467	8·111	8·218	8·074

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§ 11. The Thermal Properties of Platinum

J. F. Daniell[1] measured the **thermal expansion** of platinum and found that a rod of unit length at 62°, became 1·009926 units just about the m.p. of the metal. M. G. von Paucker observed for the coeff. of linear expansion $0{\cdot}0_4 11612$; F. C. Calvert and co-workers gave 0·0000068 between 0° and 100°; A. Tissot, $0{\cdot}0_5 8917$ between 16° and 82°; H. Fizeau, $0{\cdot}0_5 88206$, and later, for purified platinum $0{\cdot}0_5 890$ at 20°, $0{\cdot}0_5 899$ at 40°, and for the metal with 10 per cent. of iridium, $0{\cdot}0_5 884$. A. Matthiessen observed for the coeff. of cubical expansion between 7·52° and 97°, $v=v_0(1+0{\cdot}0_4 2554\theta+0{\cdot}0_7 104\theta^2)$. Observations were made by M. Thiesen, E. L. Nichols, and W. D. Flower. R. Benoit obtained values for the coeff. of linear expansion ranging from $a=(8840{\cdot}5+1{\cdot}89\theta^2)\times10^{-9}$, and $a=(8901+1{\cdot}21\theta^2)\times10^{-9}$.

H. le Chatelier gave for purified platinum, $\alpha=0{\cdot}0_4113$, and for platinum with iridium $0{\cdot}0_4105$ between 0° and 1000°; and T. Seliwanoff, $\alpha=0{\cdot}0_5975$ between 0° and about 1600°—α increases rapidly up to 150°, and thereafter, slowly. H. G. Dorsey gave $\alpha=0{\cdot}0_5815$ between 20° and —180°; G. Shinoda, $9{\cdot}9\times10^{-6}$ between 15° and 1000°; and L. J. Terneden:

	100°	200°	300°	400°	500°	600°	700°	800°
$\alpha\times10^9$.	8,950	9,050	9,175	9,350	9,530	9,750	10,000	10,441

E. Grüneisen gave:

	−150°	−100°	0°	100°	875°
$\alpha\times10^6$	7·4	7·9	8·9	9·2	11·2

and S. Valentiner and J. Wallot gave the following results, plotted in Fig. 8, for the average temp.:

	10·0°	−5·8°	−15 9°	−47 1°	−55 8°	−82·1°	−133 8°	−176·8°
$\alpha\times10^8$.	881	871	858	844	838	816	757	666

L. Holborn and A. L. Day found that a rod of unit length at 0° becomes l at temp., θ°, between 0° and 1000°, where $l=(8868\theta+1{\cdot}324\theta^2)\times10^{-9}$, or $l=l_0(1+0{\cdot}0_58868\theta+0{\cdot}0_81324\theta^2)$; K. Scheel gave for θ° between 16° and 56°, $l=l_0(1+0{\cdot}0_58806\theta+0{\cdot}0_81950\theta^2)$; between 16° and —190°, $l=l_0(1+0{\cdot}0_58615\theta+0{\cdot}0_8370\theta^2)$; between 100° and —190°, $l=l_0(1+0{\cdot}0_587490\theta+0{\cdot}0_83141\theta^2-0{\cdot}0_{11}694\theta^3)$, and between 16° and —185°, K. Scheel and W. Heuse gave $l=l_0(1+0{\cdot}0_58911\theta+0{\cdot}0_8491\theta^2)$; R. Benoit, $l=l_0(1+0{\cdot}0_58868\theta+0{\cdot}0_81324\theta^2)$; H. K. Onnes and J. Clay, between 18° and —182°, $l=l_0(1+0{\cdot}0_59053\theta+0{\cdot}0_8494\theta^2)$; or volumetrically, $v=v_0(1+0{\cdot}0_427216\theta+0{\cdot}0_71484\theta^2)$. J. B. Austin studied the subject. F. Henning observed that the changes in length of metre rods of platinum, and platinum with 20 per cent. of iridium, at 16°, were, respectively, —1·649 mm. and —1·553 mm. at —191°; +2·158 and +2·006 mm., at 250°; 4·623 and 4·321 mm., at 500°; 7·254 and 6·813 mm., at 750°; and 10·051 and 9·483 mm., at 1000°.

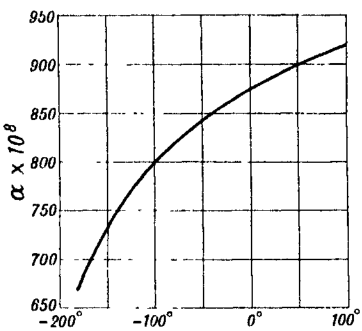

FIG. 8.—The Effect of Heat on the Coefficient of Thermal Expansion (α).

E. A. Owen and E. L. Yates measured the thermal expansion of the space-lattice of platinum up to 600°, and obtained for the coeff. of expansion at θ°, $\alpha=\alpha_0(1+0{\cdot}0_479080\theta+0{\cdot}0_838170\theta^2-0{\cdot}0_{11}79450\theta^3+0{\cdot}0_{14}29430\theta^4)$ which is in close agreement with the generally-accepted values for the material taken as a whole.

E. Grüneisen found changes in the mean coeff. of thermal expansion by pressures of 1 and 1000 kgrms. per sq. cm. to be, respectively, $8{\cdot}01\times10^{-6}$ and $7{\cdot}981\times10^{-6}$ between 17° and —190°, and $9{\cdot}00\times10^{-6}$ and $8{\cdot}976\times10^{-6}$ between 17° and —100°. H. Buff discussed the heat of thermal expansion. Relations between the coeff. of thermal expansion and other physical properties have been examined. For example, T. Carnelley, and E. M. Lémeray examined the relation between the thermal expansion and the m.p.; H. Siegerschmidt, between the elastic modulus and the coeff. of expansion; H. F. Wiebe, between the at. vol. and the coeff. of expansion; S. Bidwell, between the electrical resistance, the sp. ht., and the coeff. of expansion; A. Press, J. P. Andrews, S. Ratnowsky, G. F. Djang, and E. Grüneisen, between the thermal expansion, at. vol. and compressibility; and Y. Endo, the expansion and the lattice energy.

If the **thermal conductivity** of gold is 1000, C. Despretz [2] found that the value for platinum is 981·0. G. Wiedemann and R. Franz took silver=100 as standard and found for platinum, in vacuo 9·4 to 11·7, and in air, 8·4 to 9·2; P. Riess gave

10·5 ; E. Becquerel, 7·93 ; R. Lenz, 10·3 ; F. C. Calvert and co-workers, 12·15 ; and G. Poloni, 11·7 at 18·25°. N. W. Fischer found that the thermal conductivities of copper, iron, and platinum are related as 12 : 7 : 6 at 100° ; and at 220°, as 43 : 32 : 30. E. H. Hall, and E. Grüneisen and E. Goens studied the subject. W. Meissner observed the thermal conductivity of platinum to be k=0·167 cals. per cm. per degree per second at 0° ; J. H. Gray gave k=0·1861 between 10° and 97° ; and T. Barratt, 0·165 at 17°, and 0·170 at 100°. E. Hagen and H. Rubens represented the thermal conductivity at θ° between 0° and 800° by $k=k_0(1+0{\cdot}0_2364\theta-0{\cdot}0_6640\theta^2$; and R. Holm and R. Störmer, by $k=0{\cdot}699\{1+0{\cdot}000283(\theta-19{\cdot}5)\}$ between 19·5° and 1020°. P. W. Bridgman found a decrease in the thermal conductivity approximately, 1·9 per cent., for a change of press. of 12,000 kgrms. per sq. cm. ; and he gave for the press. coeff. of the thermal conductivity $-0{\cdot}0_516$. W. Jäger and H. Diesselhorst gave 0·166 at 18° and 0·173 at 100° for the pure metal, and 0·123 at 18° for impure metal. T. Barratt and R. M. Winter gave for k cals. per cm. per degree per second, 0·165 at 17° and 0·170 at 100°.

W. Swientoslawsky and S. Bakowsky [3] studied the evaporation of liquids from platinum surfaces. P. L. Dulong and A. T. Petit gave 0·0335 for the **specific heat** of platinum between 0° and 100°, and 0·0335 between 0° and 300°. H. V. Regnault obtained 0·03197 and 0·03294 between about 11° and 99° ; H. Kopp gave 0·0325 between 20° and 52° ; H. Tomlinson, gave between 0° and 100°, $0{\cdot}031980\theta+0{\cdot}0_563\theta^2$; R. Bunsen, 0·03234 and 0·032672 between 0° and 100° ; J. Joly, 0·0328 between 14° and 100° ; L. Schüz, 0·03037 and 0·03295 between 15° and 100° ; and A. Bartoli and E. Stracciati, 0·032238 between 16° and 100°. Observations were made by E. Terres and H. Biederbeck ; and K. Schulz compiled a bibliography on the sp. hts. of the metals. J. Violle obtained for the mean sp. ht. between 0° and

	100°	200°	400°	600°	800°	1000°	1200°
Sp. ht. .	0·0323	0·0329	0·0341	0·0353	0·0365	0·0377	0·0389

or, sp. ht.=$0{\cdot}0317+0{\cdot}000006\theta$. U. Behn gave for the purified metal, 0·0311 between 18° and −79°, and 0·0293 between 18° and −186° ; W. Jäger and H. Diesselhorst, 0·0326 between 17° and 100° ; W. A. Tilden, 0·0292 between 15° and −182°, and 0·03147 between 15° and 100°, 0·0338 between 15° and 435°, 0·0377 between 0° and 1000°, and 0·0388 between 0° and 1177°. L. Kunz obtained 0·0359 between 0° and 930° ; 0·0377 between 0° and 946° ; 0·0377 between 0° and 960° ; and 0·0378 between 0° and 1018°. A. Wigand working between 0° and the following temp. obtained 0·03145 at 32° ; 0·03181 at 54° ; 0·03204 at 97° ; 0·03216 at 133° ; 0·03223 at 162° ; and 0·03230 at 199° ; similarly with W. Schlett, 0·03055 at 8·37° ; 0·03072 at 9·84° ; 0·03144 at 49·36° ; 0·03118 at 50·45° ; 0·03198 at 96° ; 0·03206 at 111° ; 0·03236 at 207° ; and 0·03276 at 229° ; whilst W. P. White similarly obtained 0·03348 to 0·03355 at 500° ; 0·03423 to 0·03428 at 700° ; 0·03514 to 0·03515 at 900° ; 0·03573 to 0·03578 at 1100° ; 0·03640 to 0·03647 at 1300° ; and 0·03675 to 0·03682 at 1500°. O. Byström gave :

	0°	50°	100°	150°	200°	250°	300°
Sp. ht. .	0·032386	0·032480	0·032668	0·032950	0·033326	0·033796	0·034750

T. W. Richards and F. G. Jackson gave 0·0279 between 20·5° and −190·2° for platinum alloyed with some iridium. W. Plato gave for iridiferous platinum 0·03369 at 600°, and 0·03430 at 750°. H. Esser and co-workers gave 0·0348 between 0° and 800°. J. Dewar observed 0·0135 at −223°. W. Gaede gave for purified platinum the true sp. hts. :

	17·5°	32·0°	47·8°	62·2°	77·2°	99·2°
Sp. ht. .	0·03129	0·031456	0·031675	0·031798	0·031927	0·032046

W. P. White gave :

	500°	700°	900°	1100°	1300°	1500°
Sp. ht. . .	0·0356	0·0368	0·0380	0·0390	0·0400	0·0407

and E. Grüneisen :

	−150°	−100°	0°	100°	875°
Sp. ht. . . .	0·0275	0·0295	0·0318	0·0332	0·042

W. P. White gave $c=0{\cdot}03198+0{\cdot}0_5 34\theta$; C. S. M. Pouillet, gave $c=0{\cdot}0324+0{\cdot}0_5 4\theta$; J. W. Richards, $c=0{\cdot}032386+0{\cdot}0_6 94\theta+0{\cdot}0_6 188\theta^2$; W. Schlett, $c=0{\cdot}030595+0{\cdot}0_4 141\theta$ between 0° and 100° ; and $c=0{\cdot}030456+0{\cdot}0_4 2972\theta+0{\cdot}0_7 561\theta^2$ between 0° and 300° ; A. Magnus, $c=0{\cdot}03159+0{\cdot}0_5 58468\theta$ between 150° and 850° ; W. Gaede, $c=0{\cdot}03159+0{\cdot}0_4 136\theta-0{\cdot}0_7 28\theta^2$ for temp. between 0° and 150° ; and N. A. Jones and co-workers gave $C_0=5{\cdot}40+0{\cdot}0017T$. F. M. Jäger gave for the sp. ht., $c_p=0{\cdot}03162+0{\cdot}0_5 617256\theta+0{\cdot}0_9 233256\theta^2$.

W. A. Tilden gave 6·05 for the **atomic heat** ; U. Behn, 6·3 from 18° to 100°, 6·1 from 18° to −79°, and 5·4 from −79° to −186° ; T. W. Richards and F. G. Jackson, 5·45 from 20° to −188°, and 6·3 from 20° to 100° ; O. M. Corbino, 6·47 at 500°, and 7·37 at 1500° ; and J. Dewar, 2·63 at −223°. W. Zcidler, and F. Simon and W. Zcidler gave for the sp. and at. heats, c_p and C_p respectively :

	−255·5°	−248·66°	−237·58°	−222·5°	−191·6°	−152·0°	−64·7°
c_p .	0·00123	0·00309	0·00727	0·0131	0·0211	0·0261	0·0307
C_p .	0·239	0·604	1·42	2·56	4·12	5·09	5·99

F. M. Jäger and E. Rosenbohm gave :

	100°	300°	500°	700°	1000°	1300°	1600°
c_p .	0·03142	0·03256	0·03353	0·03421	0·03500	0·03576	0·03626
C_p .	6·298	6·537	6·785	7·037	7·421	7·816	8·210

O. M. Corbino measured the sp. ht. at constant vol. ; and L. Fabaro gave $c_p=c_v\{1+0{\cdot}0_4 63(T+273)\}$. E. Grüneisen said that the ratio of the sp. ht. at constant press. to that at constant vol. is 1·019 at 18°. W. Weber gave 0·0259 for the sp. ht. at constant vol., and he added that the temp. rises or falls by 100° if the metal be compressed or dilated, respectively, by one sixty-seventh. W. Schlett found the sp. ht. of 3 samples of commercial platinum vessels to range from 0·03118 to 0·03168 ; a cast specimen had a sp. ht. of 0·03168, when hammered to 2 mm. the value was 0·03134, and when cold-drawn to 0·5 mm., 0·03150 ; a specimen of cast platinum had a sp. ht. of 0·03188, and after annealing for 30 minutes at a white heat, 0·03145. F. M. Jäger and co-workers found the sp. ht. of annealed platinum to be 2 per cent. higher than that of the unannealed metal. E. Grüneisen found that the mean sp. ht., c_p, of platinum is increased by $0{\cdot}0_6 19$ per kgrm. per sq. cm. S. Bidwell studied the relation between the sp. ht., the electrical resistance, and the coeff. of thermal expansion ; A. H. Stuart, and O. Förster, the relation between the elastic constants and sp. ht. ; and J. Maydel, the general formula.

The **melting point** of platinum is so high that the metal was intractable in the furnaces available for melting metals during the first half of last century. W. Nasse [4] could not melt it in the hard-porcelain oven, but L. Elsner melted platinum black into small, metallic beads, and J. J. Prechtl did succeed in melting it in an oven heated by charcoal, and C. Aubel melted it in the hottest part of a charcoal blast-furnace, but W. Heraeus did not accept the evidence. V. Meyer melted the metal in a charcoal blast-furnace ; and H. Violette melted 50 grms. in a crucible made of gas-carbon heated in a fire-clay crucible in a furnace connected with a high chimney. The carbon, etc., here present would, according to J. B. Dumas, lower the m.p. of the metal. The metal does not melt in the strongest heat of a forge, although M. Faraday and J. Stodart obtained imperfect fusion ; if, however, the fuel be in contact with the platinum fusion may occur owing to the formation of silicides and carbides of platinum. The metal was fused in the oxy-hydrogen flame by E. D. Clarke, W. Maugham, A. Marcet, E. F. Dürre, and R. Hare. R. Hare melted 28 ozs. of platinum on a block of lime heated by the oxy-hydrogen flame ; and H. St. C. Deville, and H. St. C. Deville and H. Debray modified R. Hare's procedure and were able to melt a kilogram of metal with the consumption of 60 to 100 litres of oxygen. F. Reich melted platinum on a block

of magnesite by the oxy-carbon monoxide flame; and E. J. Chapman used the same source of heat. H. St. C. Deville also melted the metal in the oxy-coal gas flame; and in the alcohol flame fed with oxygen. M. Brettel melted the metal by a few seconds' exposure in the focus of a 3-foot burning lens. W. N. Hartley found that wires 0·025 mm. diameter can be melted in the flame of a candle; W. Skey melted pointed wires in the ordinary blowpipe flame; C. Féry melted thin wires in a bunsen burner. C. Féry and C. Chéneveau found that a horizontal wire heated electrically broke at 1690°, rather below the true m.p., a vertical wire similarly heated fused to a drop at 1710°; a wire held vertically in the flame of a meker burner fused to a bead at 1740°, and in the oxy-coal gas flame, the fusion temp. was between 1700° and 1750° according as an oxidizing or reducing flame was employed. This shows that the m.p. of platinum, like that of silver, depends on the nature of the atmosphere in which the fusion occurs. The subject was discussed by C. W. Waidner and G. K. Burgess. R. C. Smith observed the sintering of precipitated platinum-black occurs at about 500°. J. G. Children, P. Riess, and C. Despretz melted platinum wires heated by the passage of an electric current, and, as previously indicated, C. W. von Siemens and A. K. Huntington, and others melted the metal in an electric furnace. M. Rabinovitsch studied the glow on heating the finely-divided metal; R. Wright and R. C. Smith, the sintering of the finely-divided metal; and J. A. M. van Liempt and J. A. de Vriend, the time of melting thin wires.

The methods available for measuring high temp. were very unsatisfactory throughout the greater part of the nineteenth century; and consequently the m.p. of platinum could not be determined with precision. Thus, E. Becquerel gave 1460° to 1480°; J. Becquerel, 1560° to 1580°; R. Pictet, 1700°; H. Seger, 1725°; C. Barus, 1757°; W. Holman and co-workers, 1760°; F. Hoffmann, 1771°; T. Erhard and A. Schertel, and J. Violle, 1775°; L. Holborn and W. Wein, 1780°; H. St. C. Deville, 1900°; H. St. C. Deville and H. Debray, T. Carnelley, R. Pictet, and G. Quincke, 2000°; J. Dewar, 2100°; P. H. van der Weyde, 2200°; H. A. Mott, 2300°; and C. F. Plattner, 2534°. J. C. Hoadley found that the metal begins to melt at 1621°. The early workers discovered that the metal could be welded at a white heat, and this property enabled W. H. Wollaston to prepare compact masses of malleable platinum, and C. M. Marx, to repair injured platinum vessels. R. Spring found that many metals heated to temp. below their m.p. exhibit properties characteristic of the liquid state; thus, when cylinders of the metals with plane surfaces of contact are subjected to press. for 4 to 8 hrs. at 400°, all the metals tried, with the exception of platinum and antimony, were welded so thoroughly that if the piece be broken the fracture does not take place at the original surfaces of separation.

J. A. Harker obtained 1710° for the m.p. of platinum, but this datum is too low; L. Holborn and S. Valentiner gave 1789°, but this value is rather larger than that obtained by other investigators; L. Holborn and W. Wien gave 1780°; and L. Holborn and F. Henning, 1710°. F. Doerinckel, 1744°; O. Goecke, 1745° to 1755°; K. R. Koch and C. Dannecker, 1750°; A. L. Day and R. B. Sosman, 1755°; W. Nernst and H. von Wartenberg, 1745°; W. Holman and co-workers, 1760 °; C. W. Waidner and G. K. Burgess gave 1753°; H. E. Ives, 1764°; F. Hoffmann, 1771°; F. E. Carter, 1755°. G. Ribaud and P. Mohr gave 1762°; L. D. Morris and S. R. Scholes, 1773°; W. F. Roeser and co-workers, 1773·5°; F. H. Schofield, 1773·3°; and F. Hoffmann and C. Tingwaldt, 1773·8° for the f.p. Observations were made by O. Ruff. The temp. determinations also depend on the values assigned to the constant in the equation employed in standardizing the pyrometers.

H. St. C. Deville and H. Debray, and W. Heraeus noted the **spitting** of molten platinum during cooling owing to the liberation of absorbed gases as the metal solidifies. C. E. Mendenhall and L. R. Ingersoll found that platinum may be supercooled 370°, and that when the metal solidifies there is a momentary flash of light. J. L. Byers discussed the behaviour of platinum on cupellation.

Calculations of the m.p. from empirical equations have been made, and J. W. Richards thus obtained 1775°, and E. Brodhun and F. Hoffmann, 1771°; L. I. Dana and P. D. Foote gave 1755° for the best representative value; and W. R. Mott, W. Guertler and M. Pirani gave 1760°, and K. Scheel, 1764°. J. Johnston calculated that the raising of the atm. press. 1 atmosphere lowers the m.p., and that at a press. of 46,000 atm. platinum would accordingly melt at 27°—that is, of course, if something else did not happen. C. T. Heycock and F. H. Neville measured the lowering of the f.p. of cadmium, thallium, lead, and bismuth by about a gram-atom of platinum in 100 gram-atoms of metal. P. W. Robertson, and W. Crossley discussed the relation between the at. vol. and the m.p.; J. Johnston, the effect of press. on the m.p.; A. Stein, the relation between the electrical resistance, the at. vol., and the m.p.; T. Carnelley, and E. M. Lémeray, the relation between the m.p. and the coeff. of thermal expansion; L. P. Sieg, the relation between the m.p. and the elastic modulus; W. Braunbek, the lattice energy of melting; H. Jeffreys, the relation between the m.p. and the tensile strength; W. Herz, the relation between the m.p. and its vibration frequency; W. Widder, and N. F. Deerr, the relation between the m.p. and the latent heat of fusion; and W. Sutherland, the relation between the m.p. and the elastic constants. J. Johnston observed that if D be the density of the substance at the m.p., T, the absolute m.p., and Q, the heat of fusion per gram, then the press. required to melt platinum at 27° is $95{\cdot}1QD \log (T/27)$, or 46,000 atm.

H. Moissan[5] found that the **volatilization** of platinum readily occurs in the electric arc furnace, indeed, the metal boils and distils as readily as water does at 100°. O. J. Broch and H. St. C. Deville observed no volatilization when melted in oxygen gas; W. N. Hartley observed none in the oxy-hydrogen flame; and F. Mylius and F. Förster, and R. W. Hall found no evidence of volatilization at high temp. If the rate of volatilization of osmium at 1300° is 1000, that of platinum is 2. On the other hand, A. Knocke observed that in vacuo platinum volatilizes at 540°, but not at 538°. W. Crookes observed that an electrically heated wire volatilizes nearly half as rapidly as gold; and at 1300°, platinum lost in 2 hrs. 0·019 per cent. and in 30 hrs., 0·245 per cent., although no loss was observed at 900°; he first thought that the volatility is due to the formation and decomposition of unstable, volatile oxides, but later gave up the hypothesis. R. W. Hall said that the behaviour of platinum when heated is best explained by the hypothesis that an oxide is formed which is stable at high and low temp., but unstable at intermediate temp.—*vide infra*, action of oxygen on platinum. F. E. Carter said that an appreciable volatilization occurs at 1000°. H. St. C. Deville also said that the metal volatilizes rapidly at a temp. a little above its m.p.; and C. Zengelis, D. Balareff, H. M. O'Bryan, and A. Guntz and H. Bassett observed some volatilization below the m.p. J. Orcel said that the metal is sensibly volatile at 1300°, and rapidly at 1500°. L. Elsner also observed that the metal volatilizes to some extent when heated in the hard porcelain oven. W. Crookes observed the losses in weight when platinum is heated in air at 1300° to be:

Time .	2	6	10	14	18	22	26	30 hrs.
Loss .	0·019	0·062	0·095	0·128	0·169	0·195	0·218	0·245

but no perceptible loss occurred during 20 hrs.' heating at 900°. I. Langmuir and G. M. J. MacKay estimated the rate of evaporation of platinum, m grms. per sq. cm. per second, at different temp. on the absolute scale, T° K., and found $\log m = 14{\cdot}0 - 27800T^{-1} - 1{\cdot}76 \log T$, or:

T° K. .	1000°	1250°	1500°	1750°	2000°
Grms. loss	$8{\cdot}32\times10^{-20}$	$20{\cdot}4\times10^{-16}$	$75{\cdot}4\times10^{-n}$	$25{\cdot}4\times10^{-9}$	$1{\cdot}95\times10^{-6}$ per sq. cm. per sec.

F. Beilstein said that the loss in weight with crucibles becomes less and less with repeated ignitions, and L. L. de Koninck attributed the loss to the distillation of iridium from the alloy. R. W. Hall found the loss in some cases to be greater

after the twentieth ignition than after the first; in some cases, the crucible after a month's use ceases to lose weight. H. A. Jones and co-workers found the rate of evaporation, *m* grms. per sq. cm. per second, and the vap. press. *p* bars, to be :

°K.	800°	1000°	1500°	2000°
m	1.39×10^{-26}	6.70×10^{-20}	5.23×10^{-11}	1.24×10^{-6}
p	5.99×10^{-23}	3.47×10^{-15}	3.31×10^{-6}	9.07×10^{-2}

°K.	3000°	4000°	4800° (b.p.)
m	1.5×10^{-2}	1.2	8.9
p	1.3×10^{3}	1.2×10^{5}	1.0×10^{6}

G. K. Burgess and P. D. Sale showed that iridium is added to the platinum of crucibles for stiffening the metal, although it increases the losses in weight at temp. exceeding 900°. According to G. K. Burgess and R. G. Waltenberg, crucibles with up to about 3 per cent. of iridium have a negligible loss when heated below 900°; iron lowers the heat losses, and below 900°, ferruginous platinum may appear to gain in weight owing to the diffusion of the metal to the surface, and there oxidizing—*vide infra*, action of iron oxides on platinum. G. K. Burgess and P. D. Sale found that rhodium like iridium stiffens platinum, and reduces the volatilization of platinum above 900°. Observations were made by J. Strong, F. Mohr, E. Sonstadt, A. K. Boldyreff, G. A. Hulett and H. W. Berger, and E. Goldstein. G. C. Wittstein referred the loss to osmium, but F. Stolba pointed out that the loss in weight is greater than the amount of osmium in the platinum.

O. L. Erdmann thought that the grey film produced on platinum heated in a non-reducing bunsen flame is due to an allotropic change because he could detect no variation in weight, but A. Rémont showed that the film can be produced by heating the metal in a reducing flame and is then due to the formation and subsequent decomposition of a carbide, and in the case of burning gas, it is produced not by carbon suspended in the flame, but rather by one or more gaseous constituents of the flame. F. Stolba discussed this subject. L. Troost and P. Hautefeuille, L. Pigeon, and F. Seelheim noted that platinum volatilizes at a yellow heat in chlorine, and V. Meyer found that platinum so lost 1 per cent. in weight when heated in a current of dry chlorine at 1750°—presumably, in this case, an intermediate volatile chloride is formed. J. Strong studied the vaporization of platinum in vacuo from a tungsten filament; and O. Goche, the cathodic evaporation of platinum in a magnetic field.

P. Riess noted that when platinum wires are heated electrically material particles or dust are given off by the metal, and analogous observations were made by A. Berliner, T. A. Edison, J. Elster and H. Geitel, F. Emich, F. Fischer and H. Marx, W. D. Flower, H. Goldschmeid, F. Henning and L. Austin, L. Holborn and F. Henning, G. A. Hulett and W. Berger, S. Kalandyk, H. Kayser, V. Kohlschütter and T. Goldschmidt, J. A. M. van Liempt, O. J. Lodge, W. Muthmann and H. Hofer, R. Nahrwold, and G. Reboul and E. G. de Bollemont. L. Hamburger observed that thin volatilization films of platinum are not resolvable into particles. W. Stewart found that the loss is the same in dry or moist air; it does not occur in hydrogen even at a white-heat, and only very feebly in nitrogen; the loss decreases with decreasing press., thus in air at 760 mm., the loss in 2 hrs. was 1·65 per cent., 0·64 per cent. when the press. was 1·25 mm.; the loss in 2 hrs. in nitrogen at 760 mm. was 0·003 per cent., and at 3 mm. press., the loss was imperceptible. The loss in air is conditioned by the percentage amount of contained oxygen. I. Langmuir observed no loss in steam or in carbon dioxide at 1300°. R. W. Hall noted that the loss in weight occurs when the wires are heated in oxidizing gases, but not in reducing or indifferent gases. It is assumed that a volatile platinum oxide is formed and that the sublimed oxide, on cooling, decomposes into platinum. H. Freundlich observed that the phenomenon does not occur so readily when the platinum is alloyed with other metals. J. H. T. Roberts showed that two sets of nuclei are evolved when platinum wires are heated. The first set is gradually

eliminated with continuous heating, and they are produced by the evolution of the gases occluded by the wires. The properties of the nuclei are as follow :—

They are emitted by the wire at comparatively low temp. The minimum temp. required to produce them is lower the less the press. of the surrounding gas. They alter in size and disappear very soon after their liberation, but last longer if water-vapour has been caused to condense upon them. The ability of the wire to emit them is temporarily lost after an emission, but is slowly regained after the lapse of time. The wire immediately regains the ability to produce them when hydrogen is brought into contact with it; air, oxygen, and nitrogen do not produce this effect. If the wire has been kept at a white-heat in a vacuum for a very long time, the admission and withdrawal of pure hydrogen does not revive the power to emit nuclei in a vacuum.

The second set is dependent on the presence of oxygen about the heated wire,—these nuclei are never obtained below a certain temperature, and about this temp. they are always formed in the presence, but never in the absence of oxygen. The properties of the second set of nuclei indicate that an unstable, endothermal, and volatile platinum oxide is formed as indicated above, and this is in agreement with the following observations:

The second set of nuclei are not formed in nitrogen, hydrogen, or a vacuum, but only in the presence of oxygen. The rate of loss of weight of the metal is zero in nitrogen, hydrogen, or a vacuum. For platinum and rhodium the rate of disintegration at a given temperature is roughly proportional to the oxygen pressure; for iridium, which is very oxidizable, the rate of disintegration increases much more rapidly than the oxygen pressure. The disintegration of palladium is of a different nature and will be considered later. At low pressures of oxygen the nuclei are very small. The nuclei begin to be formed (that is, the disintegration begins) at a fairly definite temperature. The nuclei are very persistent and do not alter in size; they are unaffected by light or by an electric field.

I. Langmuir and G. M. J. MacKay, and W. R. Mott estimated the **boiling point** to be 3907°; H. A. Jones and co-workers gave 4527°; and F. E. Carter, 3910°. G. A. Hulett estimated that the **vapour pressure** of platinum at 200° is $0{\cdot}0_626$ mm. I. Langmuir and G. M. J. MacKay calculated the vap. press. of platinum, p mm. at different temp., on the absolute scale, $T°$ K., and found $\log p=14{\cdot}09-27800T^{-1}-1{\cdot}26\log T$, or:

$T°$ K. .	1000°	1250°	1500°	1750°	2000°	4180°
p .	324×10^{-20}	8910×10^{-16}	3160×10^{-12}	1300×10^{-9}	$49{\cdot}5\times10^{-6}$	76·0 mm.

J. A. M. van Liempt studied the vap. press. curves.

According to L. Arons,[6] when a bead of platinum is fused, and cooled, as the metal solidifies it emits a momentary glow owing to the liberation of the heat of fusion. J. Violle gave 27·18 Cals. per gram or 5·3 Cals. per gram-atom for the latent **heat of fusion**; G. Pionchon gave 27·17 Cals.; and J. W. Richards computed 27·8 cals. per gram, J. A. M. van Liempt calculated 5300 cals. per gram-atom. N. F. Mott studied the relation between the latent heat, the m.p., and the electrical conductivity. N. von Raschevsky, and N. F. Deerr made some observations on the relation between the m.p. and the heat of fusion. I. Langmuir and G. M. J. MacKay represented the latent **heat of vaporization** by $(128{,}000-2{\cdot}5T)$ cals. per gram-atom. F. S. Mortimer also studied the vapour pressure. A. Jouniaux said that **Trouton's rule** did not apply to platinum. C. M. Guldberg estimated the **critical temperature** of platinum to be 7000° when that of mercury is 1000°. J. J. van Laar, and M. Thiesen discussed the **equation of state** of platinum. J. Thomsen studied the **thermochemistry** of the platinum compounds. G. N. Lewis and co-workers, R. C. Tolman, and E. C. Eastman gave 10·0 for the **entropy** of platinum at 25°; W. M. Latimer gave 0·41 for the change of entropy between 200° and 900°. The internal energy and entropy were studied by K. K. Kelley, R. D. Kleeman, W. Herz, B. Bruzs, R. von D. Wegener, and E. Kordes. E. D. Eastman and co-workers discussed the thermal energy of the electrons in platinum.

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§ 12. The Optical Properties of Platinum

According to H. St. C. Deville and H. Debray,[1] the **colour** of platinum prepared by fusion is a more silvery white than is the case with the hammered metal. A. W. Wright said that the colour of thin films by transmitted light is grey with a blue tinge ; M. Faraday said grey ; W. L. Dudley, purple ; H. L. Barvir, grey ; G. T. Beilby, blue ; and A. Partzsch and W. Hallwachs, greyish-blue. A. W. Wright added that thicker films have a brown tinge, which passes through sepia-brown, brownish-yellow, yellow, and orange-yellow as the thickness of the film increases. F. Ehrenhaft said that in dry air, the dispersed particles produced by evaporation have a dark brown colour—*vide supra*, colloidal platinum. W. L. Dudley said that the incandescent vapour of platinum is blue. A. Kundt observed no dichroism in the colour of platinum.

K. Försterling and V. Freedericksz [2] found the **light absorption,** k, and the index of refraction, μ, for light of wave-length λ, to be :

λ	1·00	1·52	1·97	3·29	3·41	4·65μ
k	1·83	1·76	1·65	1·62	1·56	1·41

E. Hagen and R. Rubens gave for the extinction coeff., k in $I=I_0.10^{-kd}$, where d denotes the thickness, and I_0 and I, the intensities of the incident and emergent rays of light of wave-length λ :

λ .	0·326	0·385	0·45	0·55	0·65	0·8	1·2	2·0	2·5μ
k .	39·2	38·6	37·2	37·6	37·8	36·6	33·4	30·2	28·4

Observations were made by E. Dershem, P. Drude, H. Goldschmidt and H. Dember, L. Holborn and F. Henning, K. Lauch, M. Laue and F. F. Martens, W. Meier, A. Partzsch and W. Hallwachs, G. Quincke, C. V. Raman and K. S. Krishnan, W. Rathenau, H. von Wartenberg, W. Wien, and C. Zakrzewsky. C. Féry and M. Drecq gave 0·82 for the absorption coeff. of platinum black. J. Trowbridge and W. C. Sabine observed no selective absorption for ultra-violet light. R. Pohl found that the absorption of light is proportional to the photoelectric effect. G. B. Rizzo said that the transparency of thin films of platinum for light increases with a rise of temp., and is greater the larger is the refractoriness of the rays ; and E. Hagen and H. Rubens added that platinum is less transparent than gold and silver for visible and ultra-violet rays, but it is more transparent than these metals for ultra-red rays. Observations of the transparency of platinum films were made by H. Schuch, K. W. G. Kastner, H. Kienle and H. Siedentopf, E. van Aubel, and G. Govi. A. Kundt stated that if the velocity of light in silver is 100, that in platinum is 15·3.

The **reflecting power** of platinum, R, determined by K. Fösterling and V. Freedericksz for light of wave-length, λ :

λ . .	1·00	1·52	1·97	3·21	3·41	4·65μ
R . .	77	81	83	86	88	89 per cent.

and A. Partszch and W. Hallwachs gave for the reflecting power of electrolytic platinum, R_1, and for a film prepared by spluttering, R_2 :

λ .	0·65	1·0	2·0	4·0	7·0	9·0	11·0	14·0μ
R_1 .	66·8	72·9	80·6	91·5	95·5	95·4	95·6	96·4 per cent.
R_2 .	63·8	70·4	79·8	91·6	93·0	92·5	92·7	94·7 ,,

Observations were also made by W. J. Beekman and F. W. Oudt, P. Drude, I. C. Gardner, P. R. Gleason, A. de Gramont, E. Hagen and H. Rubens, R. Hamer, F. Henning, E. O. Hulbert, J. Königsberger, K. Lauch, W. Meier, W. A. Miller, A. H. Pfund, H. de la Provostaye and P. Desains, G. Quincke, P. Rouard, E. Schuch, H. E. Strauss, H. von Wartenberg, and W. Wien. E. P. Lewis and A. C. Hardy studied the absorption in the ultra-violet. A film of thickness $0 \cdot 0_6 23$ cm. was found by J. Moser to be a poor reflector. P. R. Gleason observed a marked reduction in the reflecting power with increasing age. C. Féry said that a surface of platinum black at 100° reflects 18 per cent. of the incident rays; K. J. Angström obtained only 0·82 to 1·25 per cent. for different regions of the spectrum; and T. Royds gave for platinum black deposited in 15 and in 3 mins., respectively, R_1 and R_2:

λ	0·8	8·7	25·5	51μ
R_1	0·17	0·59	0·93	1·1 per cent.
R_2	1·30	5·70	7·08	7·4 ,,

F. Limmer said that crystals of platinum obtained by the action of cupric chloride on spongy platinum had an unusually strong reflecting power. P. Desains studied the reflection of heat rays from polished platinum; the selective reflection was studied by H. Rubens; the changes of phase in the reflected light, by H. Kath, and J. Patterson; and the relation between the electrode potential and the optical constants, by V. Freedericksz.

K. Försterling and V. Freedericksz gave for the **index of refraction**, for light of wave-length λ:

λ . . .	1·00	1·52	1·97	3·29	3·41	4·65μ
μ . . .	3·42	4·71	5·92	7·50	8·82	10·90

and W. Meier:

λ .	257·3	274·9	325·5	361·1	398·2	441·3	508	668$\mu\mu$
μ .	1·171	1·294	1·275	1·375	1·735	1·398	2·285	2·913

Observations were made by E. van Aubel, H. Barvir, E. Dershem, P. Drude, W. Eisenlohr, E. Hagen and H. Rubens, S. Haughton, A. Kundt, K. Lauch, M. Laue and F. F. Martens, G. Quincke, P. A. Ross, D. Shea, W. Voigt, H. von Wartenberg, and C. Zakrzewsky. B. Pogany found for films of thickness d, the following indices of refraction, μ:

d .	1·4	2·6	4·9	7·0	11·7	16·8	20·0$\mu\mu$
μ .	3·45	3·17	2·65	2·25	2·16	2·10	2·04

J. H. Gladstone calculated 26·01 for the **refraction equivalent** of platinum in $PtCl_4$; N. Kurnakoff, 11·9 to 16·7 for platinum in $PtCl_2.4NH_3$; 16·1 to 21·0, in $Pt(NO_3)_2Cl_2.4NH_3$; 24·7, in K_2PtCl_4; and 37·7, in Na_2PtCl_6.

The **birefringence** was studied by A. Kundt, and F. Kaempf. H. Rumpelt said that the double refraction cannot be regarded as a consequence of mechanical deformation. J. Thibaud and co-workers observed no evidence of the polarization of a beam of electrons by crystal-reflection. J. B. Nathanson studied the interference fringes of thin films. D. F. J. Arago observed that the light emitted by glowing platinum is partially polarized vertically to the plane of emission. Measurements of the **polarization** were made by H. de la Provostaye and P. Desains, W. von Uljanin, K. Försterling, A. Lallemand, R. A. Millikan, M. Laue and F. F. Martens, H. Knoblauch, W. Möller, and C. W. Waidner and G. K. Burgess. W. von Uljanin found that platinum exhibits a feeble **dispersion** in the region 2μ, and the subject was studied by C. Zakrzewsky, P. Zeeman, J. Bauer, and B. Dessau; and the transmission of light by thin films, by H. Kienle and H. Siedentopf.

M. Cau [3] discussed the magneto-optical effect, and B. Pogany, the Faraday effect with spluttered films.

According to H. F. Weber,[4] the ratio of the **emissivity** of platinum to that of

silver is 1·032 at 100°; H. de la Provostaye and P. Desains gave 3·69 to 3·81; and L. Graetz, 3·2. H. de la Provostaye and P. Desains observed that if the emissivity of soot is 100, that of rolled platinum is 10·74, and of polished platinum, 9·09. E. Hagen and H. Rubens found the emissivity of platinum at 170° for wave-length 4μ, is 8·5 per cent., and for wave-lengths 8μ, 12μ, and $25{\cdot}5\mu$, respecpectively, 4·6, 3·5, and 2·82 per cent. For wave-length $25{\cdot}5\mu$, the emissivities at different temp. are:

	170°	220°	300°	600°	900°	1200°	1500°
Emissivity . .	3·49	3·68	4·04	5·40	6·86	8·34	9·84

The change in the emissivity for wave-lengths 26μ and $8{\cdot}85\mu$ with temp. is greater than the value calculated from the electrical behaviour. C. Davisson and J. R. Weeks studied the relation between the emissivity and the electrical resistance. W. W. Coblentz's results for the isochromatic radiation energy of platinum are summarized in Fig. 9. E. Bauer and M. Moulin found the emissivity, for angles less than 40°, is nearly constant, but it increases for greater angles. Observations were also made by M. Czerny, H. A. Erickson, E. Furthmann, W. Giess, M. S. Glass, E. Hagen and H. Rubens, A. L. Helfgott, F. Hoffmann, M. Kahanowicz, G. Liebmann, L. L. Lockrow, F. Paschen, F. Rossetti, R. W. Sears and J. A. Becker, V. A. Suydam, A. M. Tyndall, W. von Uljanin, and A. G. Worthing. H. Cassel and E. Glückauf, and T. B. Rymer studied the effect of oxygen on the thermionic emission.

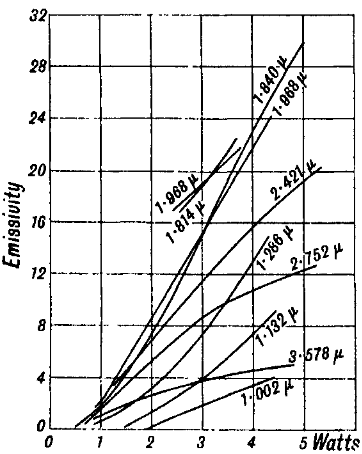

FIG. 9.—The Isochromatic Emissivity Curves of Platinum.

M. Geiseler noticed that platinum glows when heated in the oxy-hydrogen flame, and A. Crova, and E. Becquerel, that glowing platinum radiates energy like carbon, lime, and porcelain. A. Smithells, and V. B. Lewes observed that the glow of platinum is not exceeded by the glow of the carbon particles in hydrocarbon flames. G. Fletcher found that an electrically-heated platinum wire glows more strongly in air containing hydrocarbons than in air alone. P. Desains and P. Curie, and J. Meunier found that platinum can be maintained incandescent in a current of coal-gas and air even though no flame is present; he also showed that the property depends on the composition of the mixture. If a platinum wire is first cleaned with hydrochloric acid and then heated, it loses the property of remaining incandescent; if, however, it is passed between the fingers it regains that particular property because it takes up saline matter from them. This saline matter can be removed from the fingers by washing them in acidified distilled water, but not with soap and water. Thus, platinum itself is not responsible for the incandescence, but rather the saline matter which is on its surface. C. Braun noted that during the slow cooling of incandescent platinum, it retains its glow more intensely than does porcelain. C. Killing observed that a trace of platinum in thorium gas-mantles favours the incandescence as in the case of a trace of ceria. H. F. Weber observed that platinum emits a grey glow at about 360°; R. Emden said that with impure platinum the glow begins at about 404°, and with the purified metal at 408°. Observations were also made by E. L. Nichols, F. Stenger, G. Liebmann, J. le Bel, and J. Könisberger and K. Schilling. G. A. Shakespear studied the emission of heat rays from platinum. J. T. Bottomley found the heat radiated from a platinum wire at 408° is 0·3788 cal. per sq. cm. per sec., and at 505°, it is 0·07261 cal. per sq. cm. per sec. when the temp. of the surrounding air is 15°.

E. L. Nichols investigated the character and intensity of the rays from platinum glowing at different temp., and found the intensities of the spectral lines of the emitted light, on Kirchoff's scale, to be :

	1294°	1238°	1188°	1081°	901°
609 (red) *B*-line . .	1·7071	0·9470	0·5512	0·0922	0·0097
1017 (yellow) *D*-line . .	1·0000	0·5147	0·2774	0·0382	0·0013
1629 (green) *E*-line . .	0·1086	0·0512	0·0238	0·0019	—
2241 (blue) *F*-line . .	0·0391	0·0176	0·0061	0·0002	—
2853 (indigo) *G*-line . .	0·0160	0·0071	0·0017	—	—

J. Violle represented the intensities, l, at a temp. $\theta°$, by $\log l = -8\cdot244929 + 0\cdot011475\theta - 0\cdot0_5 2969\theta^2$. F. Paschen obtained for the total emission, E, of energy at

	523°	723°	923°	1123°	1323°	1523°	1723°
E . . .	3·954	26·45	110·7	340·8	839·8	1769	3451

The results are plotted in Fig. 10 along with those of J. Stefan, H. F. Weber, and F. Rossetti. Observations were also made by M. Czerny, C. Féry, P. D. Foote, L. Graetz, E. Hagen and H. Rubens, W. A. Harwood and J. E. Petavel, F. Henning, F. Henning and W. Heuse, L. Holborn and F. Kurlbaum, E. P. Hyde, R. Lucas, O. Lummer and F. Kurlbaum, O. Lummer and E. Pringsheim, W. Möller, M. von Pirani, J. Pohl, A. Schleiermacher, B. S. Srikantan, C. W. Waidner and G. K. Burgess, and O. Wiedeburg. L. A. du Bridge, E. Brodhun and F. Hoffmann, J. Patterson, H. Schmidt and E. Furthmann, A. T. Waterman, and A. G. Worthing, studied the emissivity of thin films of platinum ; J. E. Petavel, the scattering of heat rays by platinum at a high temp. ; B. W. Bradford, the thermionic emission during the oxidation of carbon monoxide ; and P. Jez, and S. Kalandyk, the thermionic emission in the vapour of iodine when the increased effect is attributed to the formation of a film of platinic iodide. The thermionic emission of electrons was studied by H. A. Barton, A. K. Brewer, H. Cassel and E. Glückauf, J. F. Chittum, C. Davisson and L. H. Germer, H. A. Erikson, W. D. Flower, R. H. Fowler, K. Fredenhagen, T. H. Harrison, L. L. Lockrow, H. H. Potter, G. Ribaud, O. W. Richardson, T. B. Rymer, B. S. Srikantan, A. T. Waterman, H. A. Wilson, and A. G. Worthing. E. Müller found that the emission from glowing platinum in hydrogen, iodine, or chlorine, unlike that in oxygen or nitrogen, decreased with time and showed a decreasing sensitiveness towards press. changes. The high results in hydrogen, iodine, and chlorine were attributed to chemical changes. P. Jez, R. A. Nelson, M. Wolfke and J. Rolinsky, and S. Kalandyk, studied the positive and negative emission from incandescent platinum in an atm. of iodine, bromine, and chlorine; and A. K. Brewer, the effect of ammonia on the emission of positive ions by platinum. C. Sheard studied the increase of positive thermionic currents from platinum wires in high vacua, produced either by heating the wire, whilst earthed, to a higher temperature than that at which the ionization is subsequently measured, or by heating it, whilst charged to a negative potential, to a temp. sufficient to cause it to discharge negative electricity, in dry air at atmospheric pressure, when the earthed wire is heated to various temperatures, there are two maxima, one after previous heating at 654° and the other at 756°. The negative emission from the wire when heated and charged negatively becomes appreciable at 760°. The results are interpreted on the theory that, on heating the

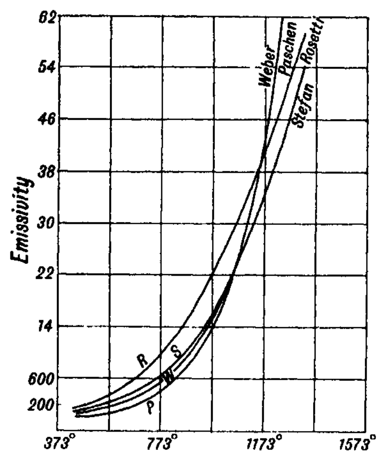

FIG. 10.—The Effect of Temperature on the Emissivity of Platinum.

wire, decomposition of a molecule AB occurs with production of two ions, A positively and B negatively charged, A being expelled or stored up, later to be expelled when an electric force is applied. At higher temp. B loses its electron. It is necessary to assume the presence of at least two substances capable of so producing ions on heating. By heating the wire in the flame of a Bunsen burner, an increased positive emission is also obtained, probably in part due to the removal of a surface material incapable of producing ions and in part due to the hydrogen absorbed, owing to its affinity for electrons. Heating in carbon dioxide decreased, if anything, the positive emission. The decay with time of the positive currents at different temperatures showed the existence of two sources of ions, the first source decaying according to an exponential law, and the second increasing to a maximum before decaying. A. M. Tyndall and G. C. Grindley found that the electrons emitted by an incandescent platinum wire, when removed from the vicinity of the particles, attach themselves to molecules and give rise to normal ions of the same mobility as those produced by polonium. The positive emission is complex, and although the greater number have mobility of 1·4 cm. per sec. per volt per cm. the mean value is of the order of 1·1. It is concluded that positive ions are emitted either as small metallic clusters or as atoms, many of which cluster before reaching the observation chamber, that the uncharged particles are metallic clusters ranging from atomic size to metallic dust, and that their growth and subsequent coagulation are responsible for the blackening of filament lamps. W. H. Crew studied the effect of light. The thermionic emission of positive ions was studied by F. Horton, L. Weissmann, H. A. Erikson, H. A. Wilson, C. Grieb, and L. L. Barnes; and G. I. Finch and A. W. Ikin found that the catalytic activity of films of platinum is connected with electrical activity. The thermionic emission of electrons from oxide-coated platinum was studied by L. H. Germer, C. Davisson and L. H. Germer, and H. E. Ives and T. C. Fry; and the thermionic constants, by H. L. van Velzer.

Platinum chloride yields a **flame spectrum** which, according to J. Formanek,[5] is of short duration. According to A. Gouy, the band spectrum of platinic chloride in the bunsen flame stretching from the red to the violet, is due to platinous chloride. The 16 bands form two groups: The one on the right, at the violet end, is very striking, that on the left is very feeble; some bands have black lines running through them. Some bands are visible in the region above the inner cone of the flame. W. N. Hartley observed no spectrum in the oxy-hydrogen flame; and W. F. Meggers and O. Laporte, and L. H. G. Clark and E. Cohen, the under-water spark spectrum.

J. Formanek observed that platinic chloride furnishes a **spark spectrum** even with a feeble spark. A. J. Angström first examined the spark spectrum of platinum, and after him came D. Alter, A. Masson, V. S. M. van der Willigen, T. R. Robinson, and W. A. Miller; and measurements were made by G. Kirchhoff, W. Huggins, and R. Thalén. According to J. Formanek, the principal lines are the green or α-line 5476; and the green lines 5390, and 5368(ϵ), 5302(β), 5227(δ), 5060(γ); the blue line 4879; and the indigo-blue lines 4553, 4442, 4415, 4392(η), and 4327(ζ)—illustrated in Fig. 11. The spark spectrum was also examined by W. E. Adeney,

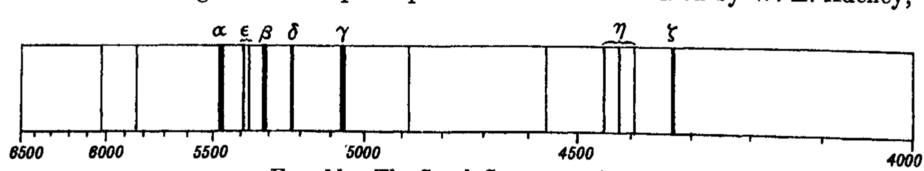

FIG. 11.—The Spark Spectrum of Platinum.

L. and E. Bloch, L. de Boisbaudran, R. Colley, E. Demarçay, F. Exner and E. Haschek, H. Finger, W. Gibbs, C. E. Gissing, A. Hagenbach and H. Konen, W. N. Hartley, W. N. Hartley and H. W. Moss, H. G. Howell and G. D. Rochester,

G. T. Globe, P. Joye, G. Kail, P. Lewis, J. N. Lockyer, B. A. Lomakin, F. McClean, H. W. Morse, H. Nagaoka and co-workers, H. Oyama, W. Spottiswoode, and E. Symons; and the under-water spark spectrum, by L. H. G. Clark and E. Cohen, and E. O. Hulbert. The **arc spectrum** was studied by J. M. Eder and E. Valenta, F. Exner and E. Haschek, S. Tolansky and E. Lee, A. Hagenbach and H. Konen, A. C. Haussmann, H. Kayser, M. Kimura, J. J. Livingood, W. F. Meggers, H. A. Rowland and R. R. Tatnall, and E. Symons; the **ultra-violet spectrum,** by G. Berndt, L. and E. Bloch, H. Buisson and C. Fabry, F. Exner and E. Haschek, G. Kail, R. Lang, J. C. McLennan and A. B. McLay, A. Miethe and B. Seegert, and V. Schumann; the electrode light, by W. von Bolton; the mechanism of the spark discharge, by S. R. Milner; the influence of the medium, by P. G. Nutting, and H. Finger; the self-induction, by E. Néculcéa, P. Joye, and G. Berndt; and the most sensitive lines for the spectroscopic detection of platinum by W. Gerlach and co-workers, and H. de Laszlo. The effect of *pressure* was studied by W. J. Humphreys; and the **Zeeman effect,** by A. C. Haussmann, and J. E. Purvis. The **series spectra** or the numerical relations amongst the spectral lines, or **series spectra,** were examined by G. Ciamician, A. Dauvillier, C. C. Kiess and O. Laporte, O. Laporte and D. R. Inglis, R. de L. Kronig, J. E. Mack, P. G. Nutting, P. J. Ovrebo, E. Paulson, and C. P. Snyder. The solar spectrum was examined for platinum lines by E. F. Baxandall, C. C. Hutchins and E. L. Holden, H. A. Rowland, etc.—*vide supra*, the occurrence of platinum in the sun.

The **absorption spectrum** of the vapour was studied by J. C. McLennan and co-workers, G. D. Liveing and J. Dewar, W. F. Meggers and O. Laporte, and C. A. von Welsbach. According to J. Formanek, the absorption spectrum of soln. of platinum salts is not characteristic in the sense of being used for qualitative tests. There are absorption bands in the blue and violet. Aq. soln. of potassium chloroplatinate give a pale band about 4860, and bands in the blue and violet. Platinum salts do not react with tincture of alkanna. The colour and spectra of the platinum salts were studied by G. B. Buckton, A. Hantzsch, N. Kurnakoff, C. A. Martius, N. Orloff, R. Samuel, R. Samuel and A. R. R. Despande, J. Schoras, and L. Wöhler and W. Witzmann; and of colloidal solutions by A. T. Williams. The **fluorescence** and **fluorescent spectrum** of the platinocyanides of the alkalies and alkaline earths was studied by E. Becquerel, J. Beuel, R. Böttger, D. Brewster, D. Cernez, J. H. Gladstone, E. Hagenbach, H. Jackson, H. Lehmann, E. Lommel, G. G. Stokes, and E. Wiedemann.

The K-series of the **X-ray spectrum** [6] includes lines of wave-lengths ($A=10^{-8}$ cm.): $\alpha_1\alpha$(or L_1–K), 0·18523; $\alpha_2\alpha$(or L_2–K), 0·19004; $\beta_1\beta$(or M_3–K), 0·16370; $\beta_2\gamma$(or $N_{5,6}$–K), 0·15887 with the absorption limit $K=0·1581$. The K-series was studied by M. de Broglie, J. C. Bryce, J. M. Cork and B. R. Stephenson, A. Dauvillier, G. B. Deodhar, E. Dershem, W. Duane and co-workers, F. Ingelstam, A. J. M. Johnson, H. Kulenkampff, K. Lang, J. E. Lilienfeld and H. Seemann, F. H. Loring, J. E. Mack and J. M. Cork, G. Rechou, J. S. Rogers, J. Schrör, H. Seeman, M. Siegbahn and E. Jönsson, J. Thibaud and A. Soltan, and E. Wagner. The L-series has the lines, $\alpha_1\alpha(M_1$–$L_1)$, 1·31008; $\alpha_2\alpha^1(M_2$–$L_1)$, 1·32121; $\beta_1\beta(M_2$–$L_2)$, 1·11722; $\beta_2\gamma(N_3$–$L_1)$, 1·09950; $\beta_3\phi(M_3$–$L_3)$, 1·009950; $\beta_4\phi(M_4$–$L_3)$, 1·1398; $\beta_5\zeta(O_1$–$L_1)$, 1·0701; $\beta_6\iota(N_7$–$L_1)$, 1·1398; $\beta_7\lambda(O_5$–$L_1)$, 1·0785; $\beta_8(M_1$–$L_3)$, 1·0928; $\beta_9(M_1$–$L_3)$, 1·0519; β_{10}, 1·0570; $\gamma_1\delta(N_4$–$L_2)$, 0·95545; $\gamma_2\chi(N_6$–$L_3)$, 0·9317; $\gamma_3\chi(N_5$–$L_3)$, 0·9256; $\gamma_4\psi(\psi)(O_{3,4}$–$L_3)$, 0·8950; $\gamma_5\kappa(N_7$–$L_2)$, 0·9855; $\gamma_6\theta(O_2$–$L_2)$, 0·9317; $\iota\epsilon(M_5$–$L_1)$, 1·49723; and $\eta\eta(M_5$–$L_2)$, 1·2401. Observations on the L-series were made by V. J. Andrew, P. Auger and A. Dauvillier, I. Backhurst, H. Brauns, M. de Broglie, Y. Cauchois, F. C. and L. P. Chalklin, D. Coster, D. Coster and J. Veldkamp, A. Dauvillier, E. Dershem, H. Hirata, M. J. Druyvesteyn, W. Duane and R. A. Patterson, E. Friman, H. Küstner and E. Arends, F. C. Hoyt, S. Idei, A. Jönsson, S. Kaufman, S. Kawata, K. Lang, R. Ledoux-Lebard and A. Dauvillier, E. Olsson, J. S. Rogers, J. Schrör, J. Veldkamp, E. Wagner, D. L. Webster, J. H. Williams, M. Wolf, and J. Zahradnicek. The M-series includes

the lines M_5N_5, 4·407 ; M_3N_3, 5·484 ; β^{11}, 6·011 ; β^{11}, 6·030 ; α^{11}, 6·223 ; M_1N_1, 6·250 ; M_3N_7, 6·663 ; M_1N_5, 8·012 ; α_1, 6·049 ; β_1, 5·831 ; β_3, 5·649 ; γ_1, 5·329 ; γ_2, 4·733 ; and γ_3, 4·623. E. Dershem, E. Hjalmar, F. L. Hunt, A. J. M. Johnson, E. Lindberg, T. H. Osgood, E. G. Purdom and J. M. Cork, and R. A. Rogers, studied the *M*-series ; E. Lindberg, T. Magnusson, and J. Thibaud and A. Soltan, the *N*-series ; and C. G. Barkla, the J-phenomena. Observations on the X-ray spectra were made by W. Duane and co-workers, M. Siegbahn and co-workers, A. Dauvillier, E. Hjalmar, and G. Wentzel. The atomic levels were studied by H. R. Robinson ; and A. E. Sandström.

When the **X-rays** act on platinum, R. Whiddington,[7] R. Berthold, A. P. Weber, H. Murawkin, and J. C. Chapman observed that secondary radiations are emitted, which, according to A. Bestelmeyer, have a velocity of $9{\cdot}6\times10^9$ cms. per sec. ; and, according to P. D. Innes, have a velocity of $6{\cdot}1\times10^9$ to $7{\cdot}5\times10^9$ for soft X-rays, and $6{\cdot}4\times10^9$ to $8{\cdot}1\times10^9$ cms. per sec. for hard X-rays. J. Laub found a maximum velocity with the use of 24,000 volts for the production of the X-rays. J. Thibaud studied the emission of positrons by the action of γ-rays on platinum. The emission of X-rays was studied by O. W. Richardson and F. S. Robertson, J. A. Baker, U. Nakaya, C. S. Brainin, and F. C. and L. P. Chalklin ; H. W. Edwards, and S. D. Gehman, the reflection of X-rays from platinum ; and E. Dershem, the refraction of the rays. The absorption coeff. for X-rays was measured by I. Backhurst, C. G. Barkla, C. G. Barkla and C. A. Sadler, G. Fournier and M. Guillot, K. Grosskurth, A. Ianitizky, F. K. Richtmyer, L. M. Alexander, R. A. Houstoun, and G. W. C. Kaye. J. A. Becker observed that a magnetic field of 18,000 gauss has very little effect on the absorption of X-rays of short wavelength. The penetrating power of X-rays was studied by J. M. Adams, S. Egbert, E. Hupka, and H. B. Keene ; T. E. Aurén, and S. J. M. Allen, the absorption ; E. Dershem, the refraction ; C. Davisson and C. H. Kunsman, R. W. James and G. W. Brindley, A. Rusterholz, and H. E. Strauss, the scattering of the rays ; S. D. Gehman, and H. E. Strauss, the reflecting power ; E. Dershem, the dispersion of the rays ; H. Mark and L. Szilard, the polarization ; J. Thibaud, the refraction ; the intensity of the rays, by A. Bouwers, W. Friederich, and A. Roiti ; the magnetic spectrum of the rays, by A. Bestelmeyer ; the fluorescence of the rays, by W. Kaufmann, and E. Marx. S. K. Allison, and H. R. Robinson studied the electron levels of the X-ray spectral lines ; the effect of a magnetic field on the absorption of X-rays ; and R. Schwarz and M. Klingenfuss, the effect of X-rays on the catalytic activity.

H. Hertz [8] observed that the **cathode rays** will pass through thin platinum foil. O. von Bäyer found that platinum black reflects the cathode rays very feebly. The action of the cathode rays on platinum was also studied by P. Lenard, A. Becker, W. Kohl, H. W. Langenwalther, J. J. Thomson, and E. Gehrcke and R. Seeliger. L. Tonks observed the anchoring of the cathode spot in discharge tubes by platinum projecting through a mercury surface. E. Dershem, and G. P. Thomson studied the diffraction of the rays by thin films of platinum ; H. W. Edwards, the intensity of the rays. N. Campbell found that the ionization produced by cathode-rays in falling on platinum can be very greatly reduced by prolonged heating of the metal in a vacuum or in oxygen. The heating first produces no effect, then there is a sudden large change, followed by a slow change, of which the end is never reached. It is probable that ultimately the platinum would not be ionized at all by cathode-rays of less than 40 volts' speed. The metal can be put back into its initial state by bombardment with cathode-rays of 100 volts' speed in a pressure of gas below 0·01 mm., but mere contact of the gas or vapours does not restore it appreciably. This restored condition, however, is much less permanent than initially, and a few minutes' heating, instead of a few hours', brings the sudden change. Thus, the same treatment which reduces greatly thermionic and photoelectric effects reduces also the ionization produced at a metal surface by cathode-rays. It is assumed that hydrogen is present in the

metal in two forms, first, condensed on the surface, and, secondly, dissolved in the interior, the sudden diminution of the ionization by heating corresponding with the abolition of the surface layer and the further gradual diminution to the progressive removal of the dissolved gas. The temporary restoration of the surface by the electric discharge is attributed to a surface "double layer." V. Kohlschütter found that when exposed to the **canal rays,** platinum splutters similarly to what it does when used as cathode in the discharge tube, and the action is greater in air than it is in hydrogen. A. J. Dempster, and K. P. Jakovleff studied the absorption of canal rays by platinum. S. C. Roy, J. T. Tate, and K. S. Woodcock studied the emission of electrons by platinum. N. Piltschikoff studied the **Moser rays ;** S. Matthes, the δ-radiation of platinum. The action of the so-called **n-rays** was studied by E. Bichat, R. Blondlot, and J. Meyer; and H. Mayer, **alkali ions.** A. Remelé noted that a heated platinum wire emits rays which will pass through paper and affect a photographic plate. J. A. le Bel studied the radiations from a heated platinum wire.

According to F. Paschen,[9] and K. Siegl, when platinum is exposed to **radium rays** it furnishes a secondary radiation. When small quantities of platinum are dissolved in conc. soln. of uranium nitrate, or a radium salt, and the platinum is separated by chemical means, it has acquired a radioactivity—*induced radioactivity*—which gradually disappears. The phenomenon with radium was studied by K. A. Hofmann and co-workers, P. Curie and A. Debierne, F. Soddy, T. Tommasina, and R. J. Strutt; with actinium, by O. Hahn; and with thorium emanation, by E. Rutherford and F. Soddy, and F. von Lerch. A. Fischer obtained a solid soln. of the radioactive material and platinum. The diffusion of radium-B and -C was studied by L. Wertenstein and H. Dobrowolska. The emission of α-, β-, and γ-rays by platinum was studied by N. R. Campbell. E. Marsden and H. Richardson found that the speed of the **α-rays** of radium is retarded by platinum, and the action of the α-rays on the metal was studied by J. E. Henderson and E. Gideon, E. O. Lawrence and co-workers, H. A. Bumstead and A. G. McGougan, H. R. von Traubenberg, and N. R. Campbell. L. Meitner studied the scattering of α-rays by platinum; and J. A. Crowther, W. H. Bragg, W. H. Bragg and R. D. Kleeman, and B. Kucera and B. Masek, the absorption of α-rays. T. I. Campan studied the gas ionization, and secondary emission by impact of positive ions on platinum. E. Badareu, T. I. Campan, H. A. Erikson, R. A. Nelson, O. W. Richardson and C. Sheard, S. Rosenblum, and E. Rudberg studied the emission of positive ions from platinum; G. E. Read, the reflection; Y. Sugiura, the diffraction; and R. W. Gurney, the scattering of positive ions. G. Hoffmann studied the α-ray activity; and G. E. Read, the reflection of positive rays; M. S. Livingston and co-workers, the artificial radioactivity. B. Sabat noted that the electric resistance of platinum is increased in the presence of radium bromide; and H. Dember, that the photoelectric sensitiveness of platinum to light is augmented by exposure to α-rays. W. Wilson observed that a homogeneous beam of **β-rays** becomes heterogeneous when passed through thin platinum foil. The absorption of β-rays by platinum was studied by S. J. Allen, J. A. Crowther, G. Fournier, V. J. Laine, J. S. Lattès and G. Fournier, J. A. McClelland, and J. Thibaud; and the emission of cathode rays, by A. M. Tyndall and G. C. Grindley, O. Klemperer, H. H. Potter, and E. Warburg. O. von Bäyer studied the effect of platinum on the β-rays from thorium-A; H. Gaertner, the diffraction of electrons by platinum; and C. Boeckner, and H. E. Farnsworth, the radiation from the metal bombarded by slow electrons; O. W. Richardson and K. T. Compton, the latent heat of "evaporation" of electrons; C. C. van Voorhis and K. T. Compton, heats of condensation; C. Davisson and L. H. Germer, J. Thibaud and co-workers, J. J. Trillat and T. von Hirsch, J. V. Hughes, G. P. Thomson, and D. A. Richards, the diffraction of electrons; E. Rupp, the polarization of electrons; and H. R. Robinson and C. J. B. Clews, the energy levels of electrons. N. Ahmad, and E. Stahel and W. Johner studied the absorption of **γ-rays.** M. S. Livingston and co-workers, E. Amaldi

and co-workers, L. Sosnowsky, F. H. Newman and H. J. Walke, E. Fermi and co-workers, and G. Hoffmann discussed the artificial **radioactivity**; and J. C. McLennan and co-workers, the artificial radioactivity produced by bombardment with neutrons. E. O. Lawrence and M. S. Livingston found but a small yield of neutrons when platinum is bombarded by deutons at 3 million volts pressure. C. A. Murison and co-workers studied the electron diffraction patterns of platinum films produced when the metal is spluttered on glass; W. V. Mayneord, H. Mayer, P. Keck and L. B. Loeb, E. Badareu, P. L. Copeland, and C. Tingwaldt, the emission of electrons; H. B. Wahlin, the emission of positive ions; and F. Schubert, the effect of re-crystallization of the metal. P. D. Foote and co-workers observed no spectra when platinum is bombarded with electrons; J. J. Trillat and M. Motz, and G. I. Finch and co-workers, the diffraction of electrons; G. E. Read, their reflection; R. W. Gurney, the scattering of the ions; A. K. Brewer, the effect of ammonia on the emission of positive ions; R. B. Sawyer, the reflection of lithium ions by platinum; C. Davisson and C. H. Kunzmann, and E. Rudberg, the scattering of electrons; J. T. Tate, the effect of the angle of incidence in the reflection of electrons; T. I. Campan, P. L. Copeland, and F. L. Mohler and C. Boeckner, the secondary emission of electrons from platinum; W. B. Mann, the emission of energy from the surface of an electrically heated platinum wire; E. Rudberg, the bombardment of the metal by slow electrons; J. E. Henderson, the discoloration of platinum by slow electrons; N. I. Koboseff and W. L. Anochin, the desorption of oxygen and hydrogen by electronic bombardment; C. C. van Voorhis and K. T. Compton, the heats of condensation of electrons from ionized helium, nitrogen, and argon; J. A. Kok and W. H. Keesom, the electronic heat capacities; M. L. E. Oliphant and P. B. Moon, the liberation of electrons by bombardment with positive rays; L. T. Jones and V. Duran, and F. Krüger and E. Taege, the effect of various gases on the photoelectric sensitiveness; and E. O. Lawrence and co-workers, and J. Thibaud, the emission of α-particles when the metal is bombarded by deutons of high speed; J. E. P. Wagstaff, and J. B. Austin, the vibration frequency of platinum; and N. Kalabuchoff, the energy of transfer from platinum to sodium chloride.

G. le Bon [10] found that platinum is sensitive to rays below $0{\cdot}252\mu$, and G. B. Bandopadhyaya, R. S. Bartlett, J. A. Becker, E. Becquerel, W. Bennewitz, E. Bodemann, R. Börnstein, A. K. Brewer, L. A. du Bridge, C. Cha, K. T. Compton and L. W. Ross, J. G. Davidson, W. Frese, E. Gehrke and L. Janicki, H. Goldschmidt and H. Dember, F. Gross, W. R. Grove, E. H. Hall, R. Hamer, W. G. Hankel, T. H. Harrison, F. Herold, K. Herrmann, F. Hlucka, R. B. Jones, N. Kalabuchoff, K. G. Kober, O. Koppuis, G. G. Kretschmar, H. Klumb, J. Kunz, W. N. Lowry, P. Lukirsky and S. Prilezaeff, Q. Majorana, H. Mayer, C. C. Murdock, K. Newbury, K. Newbury and F. Lemery, H. T. Nga, A. Partzsch and W. Hallwachs, T. Pavolini, H. Pellat, R. Pohl, G. Reboul, K. Reger, O. W. Richardson and K. T. Compton, O. Rietschel, H. R. Robinson and C. J. B. Clews, J. Robinson, S. C. Roy, E. Rudberg, E. Rumpf, E. Schaaff, S. Schlivitch, M. Sende, M. Sende and H. Simon, H. Simon, C. Stora, O. Stuhlmann, R. Suhrmann and H. Csesch, F. G. Tucker, A. W. Uspensky, E. Wasser, L. A. Welo, and A. E. Woodruff studied the **photoelectric effect.** O. Stuhlmann showed that when a beam of ultra-violet light impinges on a film of platinum so thin that its absorption can be neglected, the photoelectric effect caused by the emergent light is greater than the photoelectric effect caused by the emergent beam. Thus, the ratio of the emergent photoelectric effect to the incident photoelectric effect is greater than unity if the films are thin enough, and with platinum the ratio is constant, 1·14; but for thicker films, the ratio is less than unity. The results were confirmed by R. D. Kleeman. J. Robinson showed that the dissymmetry is the result of two effects: (i) the velocities of the electrons emitted, and (ii) the actual numbers of electrons emitted. The dissymmetry is not so marked for velocities as it is for currents. As the thickness of the film increases through 10^{-7} cm., the photoelectric effect suddenly

increases; but for films thinner than 10^{-7}, the rate is constant, and begins to diminish after the sudden increase in current has set in. The sudden rise in the photoelectric effect is attributed to the increase in the energy until it is sufficient to ionize the molecules of platinum. The thickness of film which gives the sudden rise in current is the same for slow and quick moving electrons. The orientation of the plane of polarization of the light has no influence on the dissymmetry. W. Frese noted that any treatment which renders the metal passive reduces the photoelectric sensitiveness. T. Pavolini discussed the subject. A. Coehn and K. Sperling studied the action on a photographic plate. L. A. du Bridge, C. del Rosario, and L. A. du Bridge and W. W. Roehr gave for the thermionic work function 4·99 volts, and for the true work function 4·97 volts for photoelectric currents excited by monochromatic light. The photoelectric threshold is 2486 A. O. Stuhlmann studied the subject. W. H. Crew, W. Espe, and L. T. Jones and V. Duran observed the emission of electrons from a platinum tube through which hydrogen is passing; and H. P. Walmsley, the emission of positive ions by hot platinum. C. Davisson and L. H. Germer, R. H. Fowler, O. Koppuis, and H. L. van Velzer studied the thermionic constants; E. D. Eastman, thermoelectric effects, and heat capacity of electrons; and R. Hamer gave $\lambda=2782$ for the limiting frequency of the photoelectric effect; R. Suhrmann found the intensity of the photoelectric current is $i=1{\cdot}34\times10^6T^2e^{-53610T}$. D. L. Webster studied the critical potentials; J. B. Austin, the characteristic frequency; W. Bennewitz, G. Bethe, K. Herrmann, J. Kluge, K. Reger, and M. Sende and H. Simon, the effect of adsorbed hydrogen; B. Abendroth, and A. K. Brewer, the effect of adsorbed hydrogen, nitrogen, ammonia, helium, and of temp.; H. Leupold, the effect of adsorbed ammonia; and A. E. Woodruff, and R. F. Hanstock, the effect of cold work on the photoelectric effect. C. Cha studied the relation between the incident and emergent velocities of photoelectrons emitted by thin platinum films.

According to R. Ruer and E. Scharff, an anode of platinum polarized in sulphuric acid is sensitive to light. In one case, in darkness, the e.m.f. was constant at 0·913 volt, and after half-an-hour's exposure to daylight, 0·956 volt. G. Grube and L. Baumeister observed that with the light from a mercury vapour lamp, using platinized-platinum electrodes, anodically polarized, and dipping in $2N$-H_2SO_4, the nobler the initial potential, the greater was the fall in potential. This continued in the same direction for 15 mins. after the light had been turned off, after which it rose again. Smooth platinum, coated with a golden-yellow oxide by superposition of alternating current on direct current, also showed an initial reduction of potential on exposure to light. On continued illumination, the potential rose until it was higher than the initial value and after four successive illuminations the total rise in potential was 0·179 volt. An electrode which had been strongly oxidized and kept in the dark showed no decrease in potential on exposure to light, but only a positive effect. The sensitivity of the electrode to light is weak in potassium cyanide and still weaker in sodium hydroxide. The action of X-rays is similar to that of light. V. Bjerkness studied the resonance and absorptive power of platinum for electric waves; T. Argyropoulos, and A. Wehnelt, the oscillations of a white-hot platinum wire with a repeated make-and-break; L. Arons, the electric polarization of platinum films; B. Eginitis, voltaluminescence; and J. W. Döbereiner, Nobili's rings. J. N. Frers studied the combinations Pt–CuBr; Pt–Ag_2S; Pt–Cu_2S; Pt–PbS; Pt–MoS_2; Pt–FeS_2; and Pt–ZnO as radio-detectors.

According to R. Nahrwold,[11] air in the vicinity of a glowing platinum wire increases in electrical conductivity; and J. Elster and H. Geitel found that in this way, air, coal-gas, carbon dioxide, and oxygen become positively electrified; and a wire heated to redness in air or oxygen becomes negatively charged. H. A. Wilson observed that the emission of electrified particles is greater in hydrogen than it is in air. The emission of electrified particles by hot platinum was found by A. Wehnelt to be the same if the metal is covered with calcium or barium oxide.

The subject was studied by M. S. Glass. G. H. Martin found that a hydrogen atm. favours the discharge. J. A. McClelland observed that the emission of positive ions continues up to a certain temp., and above that, at a white heat, negative ions are given off. Negative ions were found by A. Occhialini to be given off in intense electrical fields. J. A. Harker and G. W. C. Kaye found that positive ions are emitted up to 1100°, and above that temp., negative ions; the negative ionization in nitrogen at 40 mm. press. increases at first slowly and then more rapidly as the temp. rises from 1350° to 1550°; and at 1460°, by increasing the press. from 0 to 800 mm., the negative ionization increases at first quickly, and then more slowly. Observations on the subject were also made by H. A. Wilson, O. W. Richardson, E. Brunner, K. Fredenhagen, and H. P. Walmsley.

F. Richarz and R. Schenck observed that platinum foil which has been a long time in contact with decomposing ozone makes oxygen electrically conducting. O. J. Lodge noted that air which has lost the faculty of condensing water vapour by being freed from dust, will condense the vapour after being exposed to a red-hot platinum wire. G. T. Beilby observed that when a heated platinum plate, resting on glass, is exposed to the products of combustion of coal gas, rings appear on the glass, and the phenomenon is not solely thermal, but is dependent on the emission of ions which serve as nuclei for the condensation of the sulphur trioxide present as impurity in the gas. O. W. Richardson studied the discharge of electricity by hot platinum in phosphorus vapour; and L. Weissmann, and C. Grieb, during the catalysis of detonating gas. E. Warburg studied the action of ultra-violet light on the discharge, and H. T. Barnes and A. N. Shaw, the discharge from pointed electrodes.

F. Horton, and Z. Klemensiewicz attributed the emission of positive ions from hot platinum to the evolution of adsorbed gases; and H. A. Wilson referred the production of negative ions to the occluded hydrogen. According to R. Nahrwold, the fact that a platinum wire glowing feebly electrifies the air positively, and negatively if glowing brightly, is due to the burning of dust particles and other non-gaseous matter in the vicinity of the wire, and by the disintegration of the wire at higher temp. giving off charged particles of metal. When the air was replaced by hydrogen, similar results were obtained when the gas contained dust particles, or when the wire was not perfectly clean, but at higher temperatures, although a negative charge was obtained, it was much less than with atmospheric air, and at the same time it was definitely proved that the disintegration of the wire is very small in hydrogen compared with its amount in atmospheric air. When the wire, after exposure to the air, was heated in an atmosphere of hydrogen quickly, the charge was destroyed when a dull red-heat was attained. This did not occur when the wire was left in the hydrogen for some time before heating it, and the author attributes the results to the formation of oxy-hydrogen gas in the pores of the platinum, and its explosion when the wire is heated.

O. W. Richardson observed that the positive and negative ions emitted by platinum are kinetically the same as the molecules of a gas of the same mol. wt., and at the same temp. F. C. Brown made similar observations. O. W. Richardson and E. R. Hulbirt found that the sp. charge of the electrons given off by platinum at 1100° is $e/m=1{\cdot}8\times10^7$, and at 900°, $e/m=387$ and $e/H=25$, when e denotes the e.m.f.; m, the mass of the ions; and H, the mass of the atom of hydrogen. Measurements were made by J. J. Thomson, H. A. Wilson, J. C. Pomeroy, F. Horton, O. W. Richardson and co-workers, F. Deininger, and G. Owen and R. Hallsall.

W. Ogawa,[12] and H. Greismann discussed the use of platinum as a radio-detector.

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§ 13. The Electrical and Magnetic Properties of Platinum

Observations on the **electrical conductivity** of platinum were made early in the nineteenth century. H. Davy,[1] and S. H. Christie, referred the results to the conductivity of copper taken as 100, and obtained 18 to 19·8; J. Cumming gave 21·6; and observations were made by F. P. Dulk, and W. S. Harris. E. Becquerel gave 855 when that of mercury is 100; and with silver=100, E. Becquerel gave 8·042; P. Riess, 10·4; A. Matthiessen, 10·53; and L. Weiller, 10·6. Observations were also made by A. Matthiessen and C. Vogt, C. S. M. Pouillet, A. Arndtsen, E. Lenz, J. Müller, and R. Benoit. H. M. Barlow observed that Ohm's law is rigidly true for an alternating current at $1·3 \times 10^5$ amps. per sq. cm.; P. W. Bridgman's assumption that there is a variation was not confirmed.

J. Dewar and J. A. Fleming gave for the sp. **electrical resistance** of platinum, at 0°, 10,917 c.g.s. units; and for the conductivity 0·000917 mho per cm. cube at 18°. Measurements were made by K. Bädeker, G. Bainter, C. Barus, R. Benoit, H. L. Callendar, J. Clay, O. M. Corbino, J. Dewar and J. A. Fleming, O. Erhardt, A. Emo, J. A. Fleming, E. H. Griffiths, A. T. Grigorieff, T. S. Humpidge, W. Jäger and H. Diesselhorst, W. Meissner, H. Moser, G. Niccolai, E. L. Nichols, M. von Pirani, A. Schleiermacher, F. Uppenborn, L. Weiller, and A. W. Witkowsky. O. Berg gave for the resistance, *R* ohms:

	−69·8°	−11·8°	0°	58·3°	80·0°	102·4
R	$0·0_3 6902$	$0·0_3 9210$	$0·0_3 9678$	0·001190	0·001275	0·001348

K. Olszewsky gave for the resistance in ohms when the value at 0° is taken as unity:

	0°	−78·2°	−182·5°	−208·5°
R	1·000	0·800	0·523	0·453

E. Hagen and H. Rubens gave for the sp. resistance *R* and the sp. conductivity, *K*:

	170°	220°	300°	600°	900°	1200°	1500°
R	0·233	0·260	0·312	0·559	0·900	1·33	1·58
K	4·31	3·84	3·22	1·79	1·11	0·751	0·541

Quite a number of formulæ has been devised to represent the observed results. The variation of the resistance with temp. was discussed by C. Barus, R. Benoit, T. Burger, L. Cailletet and E. Colardeau, P. Chappuis and J. A. Harker, A. A. Deckert, J. Dewar, H. Dickson, W. Geiss and J. A. M. van Liempt, W. J. de Haas and J. de Boer, F. Henning and J. Otto, T. S. Humpidge, J. Königbserger and O. Reichenheim, A. Michels and P. Geels, W. Nernst, A. von Obermayer, A. Schulze, J. C. Southard and R. T. Milner, V. Strouhal and C. Barus, W. H. Keesom and A. Bijl, and C. W. Waidner and G. K. Burgess. The temp. coeff., α, at $\theta°$, for the resistance, $R=R_0(1+\alpha\theta)$, is 0·00366 according to R. Clausius; J. Dewar and J. A. Fleming gave 0·00367; L. Holborn and A. L. Day, 0·00388; W. Jäger and H. Diesselhorst, 0·0384; H. le Chatelier, 0·00325; M. von Pirani, 0·00380; F. Henning, 0·00392; C. Barus, 0·0029 to 0·003 between 0° and 100°, and 0·00222 to 0·00265 between 0° and 357°; P. W. Bridgman, 0·00387; and L. Holborn, 0·00392. L. Cailletet and E. Bouty gave 0·0030 at 0°, and 0·00342 at −94·57°. L. Holborn gave:

	100°	780°	1140°	1300°	1500°
α . . .	0·0038556	0·0039155	0·0039144	0·0039119	0·0039070

G. Niccolai obtained a linear relation for the resistance at temp. between −189° and 400°, but L. Holborn and W. Wein found that there is a bend in the curve, Fig. 12, corresponding with a parabolic formula. E. Hagen and H. Rubens gave $R=0{\cdot}154(1+0{\cdot}0024\theta+0{\cdot}0_5 33\theta^2)$; C. W. von Siemens, $R=0{\cdot}034369T^{\frac{1}{2}}+0{\cdot}00210407T-0{\cdot}2413$; H. L. Callendar, $R=0{\cdot}03771T^{\frac{1}{2}}+0{\cdot}002520T-0{\cdot}2450$; F. Henning and W. Heuse, $R=R_0(1+0{\cdot}003969520\theta-0{\cdot}0_6 64408\theta^2-0{\cdot}0_{11}517165\theta^4)$; R. Holm and R. Störmer, $R=0{\cdot}00001048\{1+0{\cdot}003695(\theta-15)-0{\cdot}0_6 598(\theta-15)^2+0{\cdot}0_{10}525(\theta-15)^3\}$; and E. Grüneisen expressed his results in terms of P. Debye's function—**1**. 13, 16. W. Tuijn, H. Moser, H. Rolnick, A. T. Grigorieff, G. Bainter, and J. T. MacGregor-

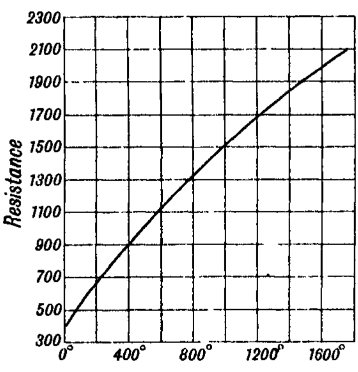

FIG. 12.—The Effect of Temperature on the Resistance.

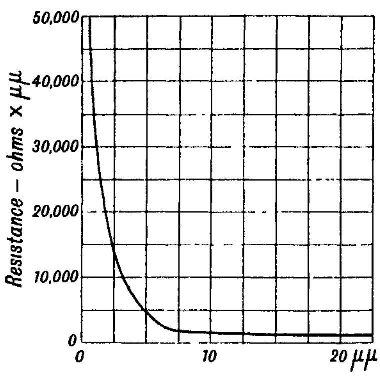

FIG. 13.—The Resistance of Thin Films of Platinum.

Morris and R. P. Hunt studied the subject; and J. M. Gaines, E. Waetzmann and co-workers, and S. Kambara and M. Matsui, resistance thermometers of platinum.

According to F. Streintz, the sp. resistance of platinum black of sp. gr. 11·6 is $R=0{\cdot}92(1+0{\cdot}001456\theta)$, a value about six and a half times as great as that of solid platinum, whereas the temp. coeff. is less than half of that of the solid metal. J. Mooser observed that the sp. resistance of samples of spluttered platinum was 11·3, 23·1, and 82·3 times greater than the platinum *en masse*, presumably owing to the formation of oxidized films on the surfaces of the granules. J. Kramer found the conductivity of thin films, produced by cathode spluttering or by vaporization, is about a millionth part of that of the normal metal. R. Deaglio, H. Kahler, Y. Maslakovetz, H. Murmann, E. Perucca, and S. Virtel studied the subject.

L. C. van Atta, R. S. Bartlett, G. Braunsfurth, A. Féry, A. W. Gauger, F. Joliot, J. Kramer and H. Zahn, E. Perucca, F. W. Reynolds, A. Riede, and K. Schtschodro, studied the conductivity of thin films; and F. Skaupy and O. Kautorowicz, the conductivity of powdered platinum under press. J. Patterson found that the sp. resistance of thin films of platinum rapidly increases as the thickness of the film decreases from $\mu\mu$ downwards. B. Pogany confirmed this, and his results are summarized in Fig. 13. A. Riede represented the conductivity, K mhos, of films of thickness x mgrms. per sq. cm. by $K=(1\cdot07x-0\cdot0005)+(0\cdot13x-0\cdot0085)$. The subject was investigated by E. Bose, R. Pohl, A. C. Longden, and J. Patterson. H. K. Onnes gave for the ratio of the resistance, R, at $T°$ K., to that, R_0, at 273·09° K.

°K.	273·09°	20·2°	14·2°	4·3°	2·3°	1·49°
R/R_0	1	0·0171	0·0135	0·0119	0·0119	0·0119

and W. H. Keesom and J. N. van Ende, J. O. Linde, W. Meissner and B. Voigt, W. Tuijn, and W. Tuijn and H. K. Onnes found that platinum did not show superconductivity at low temp. The indications point to a zero conductivity for the pure metal at absolute zero; and the small constant value observed below 4·3° K. is attributed to the presence of an impurity. The subject was discussed by C. A. Crommelin, W. J. de Haas and J. de Boer, and W. Meissner and B. Voigt. As a rule, the temp. coeff. of the electrical conductivity of a metal is greater the higher the degree of purity. R. Suhrmann found that with platinum foil between 400° and 1600°, in vacuo, the resistance increases as the gas is pumped off, it then passes through a maximum and afterwards decreases. Thus, at 926°, the resistance of platinum rose from 0·4315 to 0·4345 ohm when the metal was soaked in hydrogen, and as the gas was pumped off, the resistance passed successively through the stages 0·4498, 0·4506, 0·4494, 0·4430, and 0·4280 ohm. The relation between the resistance, R ohms, and temp. of the metal in two different states of hydrogenation is indicated in Fig. 14. The subject was studied by A. W. Gauger, K. Herrmann, L. Holborn, H. Kleine, Y. Maslakovetz, F. W. Reynolds, K. Weil, and H. A. Wilson. W. H. Stannard compiled a table of resistance; and J. D. Stranathan studied the resistance with high frequency currents. G. Szivessy found that after being heated to redness in oxygen, the resistance of platinum was increased 3·8 per cent. E. Grüneisen and E. Goens studied the application of Wiedemann and Franz's rule; F. W. Reynolds, and H. Dobretsberger, the effect of absorbed hydrogen, nitrogen, and carbon dioxide on the high frequency resistance; R. Holm and W. Meissner, the effect of oxygen on platinum films; F. W. Reynolds, the effect of oxygen, and hydrogen; R. Suhrmann, K. Weil, and H. Kleine, the effect of hydrogen. K. Kleine found that the resistance of vacuum annealed platinum increases if it is allowed to stand in air for five days. L. Holborn and W. Wien studied the action of steam on the conductivity.

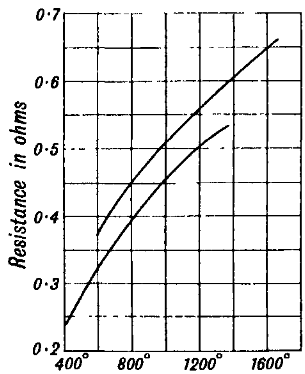

FIG. 14.—The Effect of Occluded Hydrogen on the Resistance of Platinum at Different Temperatures.

O. Feussner observed that the temp. coeff. of platinum wire generally decreases by an amount almost within the limits of experimental error when it is subject to mechanical stress. When a wire is passed through a drawing-plate to reduce its cross-sectional area, a very large decrease in the temp. coeff. occurs. P. W. Bridgman reported that the temp. coeff. between 0° and 100° of a sample of purified platinum was 0·003905, and after being subjected to a press. of 12,000 kgrms. per sq. cm., 0·003868. P. Cohn found that the resistance of platinum wire decreases with heating, and this the more rapidly the higher the temp., as indicated

in Fig. 15, and by increasing the drawing velocity the resistance is increased by about 0·1 per cent. In Fig. 15, the resistance is represented by the ordinates and the logarithm of the time, by the abscissæ. W. H. Johnson showed that an annealed metal wire should conduct electricity better than an unannealed wire, and in agreement with this, C. W. von Siemens found that the conductivity of a drawn wire increased in the ratio 100 : 100·3 by annealing at a red-heat; E. Becquerel similarly observed the ratio 100 : 101·3; and O. Chwolson found the change with a feeble heating to be —5·3 per cent., and with a strong heating +5·8 per cent. G. W. A. Kahlbaum and E. Sturm also showed that the resistance of a hard platinum wire is 0·98150, and after annealing at a red-heat, 0·97555, a decrease of 0·61 per cent. A. Heintz emphasized the fact that since the conductivity of the wire depends on its structure, measurements of the resistance should be made on specimens which have been subjected to a similar heat treatment. G. Tammann and K. L. Dreyer studied the effect of cold-work. L. Guillet and M. Ballay observed an increase of 1·6 per cent. in the resistance of the cold-worked metal when annealed at 850°. L. R. Koller noted that the decrease of a film of spluttered platinum in vacuo is due to coalescence which is retarded by the presence of gases. G. Bainter, F. Joliot, and A. Riede studied the effect of the nature of the support on the resistance; and F. Ehrenhaft and E. Wasser, the resistance of gases with a platinum aerosol.

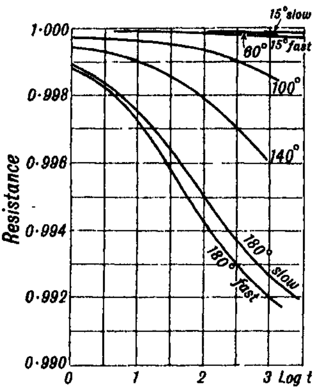

FIG. 15.—The Change in the Resistance of Platinum with Time and Temperature.

M. Ascoli observed that the resistance increased as the *elastic modulus* increased, and H. Tomlinson found that the increase of resistance per unit caused by a stress of a gram per sq. cm. is 2285×10^{-12}; and he also studied the effect of *torsion* on the resistance; and O. Feussner, and H. Rolnick, the effect of *tension*. S. Lussana found that the resistance, R ohms, decreased with an increase of *pressure*, p atm., on the metal, so that if δR denotes the change of the resistance:

p .	1	100	190	300	390	500	595	680	750
R .	5·94565	5·94422	5·94295	5·94180	5·94093	5·94016	5·93964	5·93920	5·94886
δR .		$0·0_5240$	$0·0_5237$	$0·0_5176$	$0·0_5166$	$0·0_5118$	$0·0_592$	$0·0_587$	$0·0_582$

K. Honda and co-workers studied the subject. E. D. Williamson found the ratio of the electrical resistance at 1 kgrm. and 12,000 kgrms. per sq. cm. press. is 0·9776. P. W. Bridgman obtained for the press. coeff. at 0°, —78·4°, and —182·9°, and 7000 kgrms. per sq. cm. press., the respective values $-0·0_5193$, $-0·0_5197$, and $-0·0_5234$. A. Lafay gave $\delta R/R = -0·0_5186$; E. Lissell, $-0·0_5827p + 0·0_{10}41p^2$; and S. Lussana, $-0·0_5156p + 0·0_{10}521p^2$. A. Michels and P. Geels found that at lower press. the coeff. varies more than it does with temp. P. W. Bridgman showed that the samples here employed were probably contaminated with iridium. P. W. Bridgman also gave for the fractional change in the longitudinal resistance of platinum, $1·78 \times 10^{-6}$ per kgrm. per sq. cm., and for the fractional change in the transverse resistance $0·34 \times 10^{-6}$ per kgrm. per sq. cm. The press. coeff. of the sp. resistance found by E. Grüneisen is $-0·0_5179$; by P. W. Bridgman, $-0·0_5207$; and by B. Beckman, $0·0_5150$. P. W. Bridgman obtained for platinum of a high degree of purity, with press. up to 12,000 kgrms. per sq. cm.:

	0°	25°	50°	75°	100°
R	1·0000	1·0967	1·1934	1·2901	1·3868
$\delta R/R$ 0 kgrms. . .	$-0·0_51975$	$-0·0_51950$	$-0·0_51935$	$-0·0_51915$	$-0·0_51900$
$\delta R/R$ 12,000 kgrms. .	$-0·0_51765$	$-0·0_51771$	$-0·0_51774$	$-0·0_51776$	$-0·0_51777$
$\delta R/R$ Average . .	$-0·0_51870$	$-0·0_51862$	$-0·0_51854$	$-0·0_51846$	$-0·0_51838$

S. Bidwell studied the relation between the resistance, R, and the *thermal expansion*; and A. Stein, the relation between the resistance and the *melting-point*. According to E. L. Nichols, if l denotes the length of platinum at temp. up to near the m.p., then taking the values of R and l at 0°, as unity, the corresponding values of l and R are:

l .	1·0000	1·00125	1·00489	1·01022	1·01229	1·01371	1·01495	1·01567
R .	1·0000	1·5057	2·3035	3·3533	3·7090	3·8904	4·0655	4·2005

W. Broniewsky studied the subject. The relation between the resistance and the *thermal conductivity* was studied by G. Wiedemann and R. Franz, and H. Reddemann; and W. Jäger and H. Diesselhorst observed that platinum has a greater value for the ratio thermal : electrical conductivity, and a greater temp. coeff. than corresponds with Wiedemann and Franz's rule—**3**, 21, 5. F. Streintz, and S. Bidwell studied the relation between the *specific heat* and the resistance of platinum; and N. F. Mott, the relation between the *latent heat*, the m.p., and the electrical conductivity. R. Börnstein said that the conductivity of platinum is increased by exposure to *light*; but C. W. von Siemens observed no perceptible change. The subject was discussed by C. Hausemann, and F. Weber. According to W. Jäger and H. von Steinwehr, the percentage increase in the resistance, δR, of a platinum wire—0·1 mm. in diameter, and 35 cms. in length, and total resistance 5 ohms—by the passage of a current of C ampères, as the temp. rises $\delta\theta°$, is as follows:

C . . .	0·0043	0·0196	0·0355	0·0524	0·0689	0·1000
δR . .	0	0·035	0·10	0·235	0·41	0·88
$\delta\theta$ . . .	0	0·009	0·025	0·059	0·101	0·220

The subject was studied by F. Weber. A. Broca and M. Turchini studied the resistance of platinum to *alternating currents*. A. T. Waterman, and J. W. Nicholson studied the electron theory of conduction. K. Bamberger observed no change in the resistance of platinum in a *magnetic field*, and the subject was studied by W. Kohlrausch, S. H. Christie, and P. Kapitza; and L. Grunmach found that a transverse magnetic field produces but a very small change in the resistance. F. Weigert found that a platinum wire 0·05 mm. diameter and of resistance 13·18 ohms, had a resistance of 13·311 ohms in a magnetic field of 11,500 gauss, and 13·242 ohms in a magnetic field of 16·210 ohms. N. d'Agostino observed that with a wire 0·15 mm. and 13·48 ohms resistance, the quotients x of the change in the magnetic field and the total resistance for magnetic fields of 2400, 3690, 4840, and 6510 gauss are respectively $-0{\cdot}0_525$, $0{\cdot}0_561$, $0{\cdot}0_411$, and $0{\cdot}0_420$.

J. Frenkel and N. Miroluboff, G. Borelius, H. M. Barlow, A. T. Waterman, F. Simon, H. F. Mott, and E. H. Hall studied the theory of conductivity; and Z. A. Epstein, the periodic variation of the resistance of metals with at. wts.

The heating effect of the electric current in platinum was studied by E. Becquerel,[2] G. D. Botto, J. G. Children, H. Davy, A. Farkas and H. H. Rowley, R. T. Glazebrook and co-workers, W. R. Grove, E. Lenz, J. Müller, W. H. Preece, P. Riess, A. de la Rive, M. Viard, and F. Zöllner; the use of platinum for resistance wires in electric furnaces, by G. Nordström; the development of stationary waves by wires heated by alternating currents, by A. Imhof; the effect on sounds produced by the current, by T. Argyropulos, R. M. Ferguson, and W. H. Preece; the mechanical action of the current by A. Berliner, E. Edlund, F. Exner, W. R. Grove, R. Nahrwold, G. von Quintus-Icilius, and H. Streintz; and the resistance at the contact surface of electrode and electrolyte by O. Scarpa; and R. Holm, at the contact of two surfaces; E. Branly observed the unipolar conductivity of the Ag–Mica–Pt condenser; F. Skaupy and O. Kantorowicz, the resistance of the compressed powder; H. Rohmann, the unipolar contact between two pieces of platinum wire which have been heated to incandescence for a long time in vacuo; R. Holm and R. Störmer, the resistance of platinum contacts; and

G. Hoffmann, the production of a current between two platinum plates separated a small distance by applying a difference of potential under such conditions that the intervening gas is not ionized.

The **Volta effect** of platinum against other metals—dry—was examined by J. W. Ritter,[3] who found platinum to be positive against antimony, negative against gold; T. J. Seebeck likewise placed platinum between copper and silver; and F. Polednik found the contact potential of platinum against glass to be +2·22 volts, and against fused quartz, +1·15 volts; and C. H. Pfaff, between tellurium and palladium. By frictional electricity, A. Macfarlane placed platinum between gold and tin. The subject was discussed by J. J. Berzelius, E. Dubois, E. Edlund, J. H. Gladstone and A. Tribe, J. M. Gaugain, and O. Knoblauch. The difference of potential between platinum and air was found by M. Andauer to be 0·25 volt. The e.m.f. of the Volta effect of platinum against *carbon* was measured by W. E. Ayrton and J. Perry, and W. G. Hankel; against *copper*, by W. E. Ayrton and J. Perry, F. Krüger and G. Schulz, R. Vieweg, F. Exner, W. G. Hankel, E. Edlund, A. Hagenbach, and A. Righi; against *silver*, by F. Exner, H. Greinacher, R. Vieweg, F. Krüger and G. Schulz, and W. G. Hankel; against *gold*, by W. G. Hankel, and H. Pellat; against *magnesium*, by W. E. Ayrton and J. Perry, B. J. Goosens, J. H. Gladstone and A. Tribe, and E. Obach; against *zinc*, by S. Arrhenius, E. Becquerel, F. Exner, H. Gautier, J. H. Gladstone and A. Tribe, W. Hallwachs, W. G. Hankel, M. H. Jacobi, R. Kohlrausch, and E. Obach; against *cadmium*, by W. E. Ayrton and J. Perry, and W. G. Hankel; against *mercury*, by F. Exner and J. Tuma, W. G. Hankel, R. Vieweg, H. Hörig, and C. Christiansen; against *aluminium*, by W. G. Hankel; against *tin*, by W. G. Hankel, and W. E. Ayrton and J. Perry; against *lead*, by W. G. Hankel, and W. E. Ayrton and J. Perry; against *brass*, by W. G. Hankel, and R. Vieweg; against *nickel*, by R. Vieweg, and F. Krüger and G. Schulz; against *nickel-silver*, by W. G. Hankel; against *antimony*, by W. G. Hankel; F. Krüger and G. Schulz, and G. Mönch, against *tungsten*, tantalum, iron, molybdenum; T. Terada, against *platinum* in hydrochloric acid; and against *bismuth*, by W. G. Hankel. O. W. Richardson and F. S. Robertson found the contact difference of potential with platinum at 1470° is nearly proportional to the press. of hydrogen. R. D. Kleeman and C. R. Pitts studied the sign of the electric layer away from the surface of a soln. in contact with air or a metal. J. B. Seth and co-workers studied the e.m.f. developed when platinum is in contact with a rotating steel disc; A. Coehn and co-workers, R. von D. Wegner, E. Perucca, and F. Polednik, the contact potential between platinum and insulators; B. Kamiensky, platinum and the dielectric; and M. Andauer, platinum and air. P. E. Shaw and co-workers, J. H. Jones, and W. M. Jones studied the **frictional electricity** developed with platinum.

The literature on the electrical properties of platinum here given was previously reviewed by G. Wiedemann,[4] and W. Loewenstein. The **electrode potential** of platinum was examined in a qualitative way by H. Buff, who found that in water it is feebly negative, and positive in dil. and conc. nitric acid, dil. sulphuric acid, and in conc. soln. of zinc sulphate; by C. Cappa, who found it positive in water, dil. sulphuric acid, and nitric acid; and by E. Gerland, who found it to be negative in water. H. Buff observed ordinary platinum to be negative in sulphuric acid, but positive when the metal is charged with hydrogen; E. Becquerel found the metal charged with hydrogen is negative in water, and if exposed to the action of oxygen or iodine vapour, it is positive; and W. G. Hankel noticed that in water, the polished metal is negative, and the fresh filings are positive. F. Exner and J. Tuma observed no difference of potential with purified platinum in water, sulphuric acid, or soln. of copper sulphate. I. I. Schukoff compared the effect with smooth platinum and platinum-black. N. T. M. Wilsmore found the potential in normal soln. of potassium chloride against a normal calomel electrode to be less than −1·140 volt. W. E. Ayrton and J. Perry observed the e.m.f. against distilled water is −0·285 to −0·345 volt at 16·5°; against a conc. soln. of alum, 0·246 volt;

against a soln. of sodium chloride of sp. gr., 1·18, —0·856 volt at 15·5°; against a conc. soln. of ammonium chloride, —0·057 volt; against conc. sulphuric acid, 1·300 to 1·600 volt; and against conc. nitric acid, 0·672 volt. F. Bergius observed that the potential of copper, silver, or zinc against platinum in fuming sulphuric acid decreases as water is added, and finally attains a constant value. K. Horovitz studied the effect of the acidity of H'-ion conc. of the soln.; and G. Tammann and K. Bochow, the effect of adsorbed hydrogen. F. Vles and A. Ugo measured the effect of the acidity of the soln.

W. Ostwald found the absolute potential of platinum with occluded air against $2N$-, N-, and $0·1N$-H_2SO_4 to be respectively —1·341, —1·325, and —1·219 volts; and against N-KOH, —0·492 volt. The subject was studied by K. Bennewitz and J. Schulz, V. Karpen, S. Makishima, S. Veil, W. J. Müller and K. Konopicky, I. I. Schukoff and co-workers, A. Slygin and A. Frumkin, and M. Thalinger and M. Volmer. E. Müller observed the natural potential of smooth platinum in N-H_2SO_4, and against a normal hydrogen electrode, taken to be zero, is —0·73 volt, and with platinized platinum electrode, —0·88 volt; B. Neumann gave —1·14 volt for the absolute potential of platinum coated with platinum black in N-$PtCl_4$; and F. Ott, 0·490 to 0·825 volt for platinum coated with columbium dioxide. S. Glasstone and A. Hickling studied the variation of the potential with time, in chloride soln. F. W. Küster and W. Lommel observed the potential of platinum in N-, $2N$-, $4·84N$-Na_2S to be, respectively 799, 750, and 600 microvolts; and F. W. Küster gave for the potential E volt, of soln. of n gram-atoms of sulphur in sodium sulphide, Na_2S_n, for:

n .	4·47	4·67	4·84	4·98	5·12	5·22	5·24	5·20	5·04	4·45
N- .	4	2	1	0·5	0·25	0·125	0·0625	0·03125	0·0156	0·0078
E .	0·6211	0·6087	0·6000	0·5916	0·5836	0·5758	0·5683	0·5603	0·5523	0·5411

E. G. Weischede found the electrode potential in ammoniacal $0·04N$-soln. is 0·64 volt at 20°; and in acidic soln. with 20·4 mgrms. of platinum is 100 c.c., 0·857 volt at 20°, and 0·924 volt at 60°; J. Liger, in soln. of sodium chloride and hydroxide, barium chloride, nickel sulphate, and copper salts; and A. Smits, in bromine water —**15**. 68, 6, Fig. 41. F. Giordani and B. Focaccia studied the cathodic and anodic potentials of smooth platinum in 30 per cent. soln. of potassium hydroxide. S. B. Christy observed for N-, $0·1N$-, and $0·01N$-KCy, respectively —0·40, —0·46, and —0·50 volt; B. Neumann, for soln. of potassium dichromate, —1·063 volt; dichromic acid, —1·397 volt; sodium hydrosulphate, —0·662 volt; potassium ferrocyanide, —0·593 volt; nitric acid, —1·259 volt; and neutral ferrous sulphate, —0·635 volt; and E. F. Burton, for ethyl malonate, —0·054 volt; G. Holst, in hydrazine; and J. Sambussy, in nitrobenzene. P. Bechtereff observed that the electrode potential of platinum in molten sodium hydroxide at 330° to 650° is the same as that of iron, cobalt, nickel, gold, silver, copper, constantan, or magnetite.

According to W. D. Bancroft, the potential of normal soln. of some depolarizers is as follows: potassium permanganate, 1·76 volts; chlorine in potassium chloride, 1·67 volts; manganese dioxide in potassium chloride, 1·63 volts; bromine in potassium bromide, 1·43 volts; chloric acid, 1·42 volts; dichromic acid, 1·40 volts; bromine in potassium hydroxide, 1·32 volts; perchloric acid, 1·27 volts; nitric acid, 1·26 volts; ferric chloride, 1·24 volts; chlorine in potassium hydroxide, 1·19 volts; potassium nitrate, 1·14 volts; potassium dichromate, 1·06 volts; and iodine in potassium iodide, 0·89 volts.

S. J. French and L. Kahlenberg found that the potential of platinum in N-KCl in hydrogen becomes more basic reaching a maximum and then falling off; in nitrogen, the potential becomes more basic, reaching a maximum, and then falling off; and in oxygen, the potential changes very little. Carbon monoxide, and methane alter the potential, but helium has very little effect. B. Kamiensky studied the potential in contact with an aq. soln. of potassium chloride and an emulsion of potassium xanthate and turpineol. L. Kahlenberg and J. V. Steinle

observed the single potential of platinum in $0{\cdot}5N$-Na_3AsO_4 to be 0·983 volt; in $0{\cdot}5N$-K_3AsO_4, 0·980 volt; and in N-KCl sat. with arsenic trioxide, 0·943 volt; and S. Koidzumi studied the potential of platinum in alkaline soln. containing alcohol; A. Frumkin and co-workers showed that in the alteration in the potential of platinized carbon in an atm. of hydrogen from positive to negative with increasing content of platinum, the metal in the intermediate state is uniformly at the same potential and not located at an equal number of positive and negative centres. J. Chloupek found that the potential of a platinum electrode in soln. of ortho-, pyro-, and meta-phosphoric acid, and arsenic acid, containing mixtures of manganous and manganic oxides, against a mercury sulphate electrode in $2N$-H_2SO_4, varied between 0·98 and 1·18 volt, and, at first, increased slowly with time, then decreased owing to the instability of the soln. H. V. Tartar and H. K. McClain studied the effect of an electric field; and R. Audubert, G. E. Muchin and M. I. Silberfarb, I. Lifschitz, C. Stora, G. Athanasiu, and C. Winther, the **Becquerel effect**; J. M. Ort and M. H. Roepke, the potential in dil. alkaline sugar soln.; J. Harty, the potential of a photovoltaic cell in combinations with ethyl- and phenyl-magnesium chloride; T. Swensson, the e.m.f. of a cell with a partition Pt | soln. : soln. | Pt in which one half is kept in darkness, and the other half illuminated by ultra-violet light. The electrolytes were soln. of several salts. G. Athanasiu examined the effect of radiant heat on the Pt : $PtCl_4$: Pt-cell; and G. Grube and L. Baumeister, that of light and X-rays on polarized platinum electrodes. L. V. Nikitin observed that some cells with platinum electrodes appear to be sensitive to sound.

According to C. Fredenhagen, platinum electrodes in some oxidizing soln. show a constant potential immediately after immersion, whilst in others it is variable, and this indicates that the velocity of reaction of the ions of the oxidizing soln. with the gases absorbed by the platinum is very variable. In oxidation elements, the platinum electrodes always become charged with gases; in some cases, the potential measured is entirely due to this gas charge, and is in no way conditioned by the giving up of electrons from the ion of the solution to the electrode. The magnitude of the gas charge is dependent on the $H^{\cdot}$-ion conc. in the liquid, but the potential of the oxidizing agent is absolutely independent of this. N. E. Loomis and S. F. Acree prepared platinum electrodes for use as hydrogen electrodes in 0·1HCl in determining the $H^{\cdot}$-ion concentration in reacting systems, in which the deviation from the mean is less than 0·1 millivolt. H. D. Kirschman and co-workers, D. J. Brown and J. C. Zimmer, studied the subject. F. Fischer observed that when external influences are excluded, the e.m.f. of certain open cells of the type: Cu | $CuSO_4$ soln. | Pt slowly falls to zero, and the same change takes place in a few hours if the electrolyte be agitated. Cells with mercury or silver in place of copper behave similarly, but not so with zinc. The change with the copper cell takes place only at the platinum electrode, and it is assumed that cuprous sulphate is formed from the metallic copper and the copper sulphate, this in turn involving a tendency throughout the electrolyte to the separation of copper. The copper potential is thus transferred to the platinum electrode. The part played by the cuprous sulphate is illustrated by the fact that by the use of various solutions all saturated with cuprous sulphate the platinum can be made to assume any potential between that of oxygen and that of copper. The fall in the e.m.f. of the cell is attributed to the formation of an alloy of platinum and copper which gradually becomes richer in copper as the distribution of cuprous sulphate through the electrolyte proceeds. R. Luther made observations on the same subject; and W. J. Müller and J. Königsberger found the optical properties of the platinum were not affected by the reaction in the cell, and this does not support the hypothesis that an alloy is formed. H. V. Tartar and H. K. McClain referred the electrode potential to adsorbed films; R. D. Kleeman and co-workers, the sign of the electrical layer of a soln. in contact with platinum. E. R. Smith found that the e.m.f. of a cell with the electrode reaction $PtCl_4''+2Cl'=PtCl_6''+2\epsilon$ shows reversibility;

and the platinoplatini-electrode was studied by V. F. Miller and H. Terrey, and E. R. Smith. W. M. Pierce studied the relation between current and time in a Pt–H_2SO_4 cell; F. P. Bowden, the potential changes which occur during the discharge of electricity at bright platinum electrodes in air-free, 0·2N-H_2SO_4 sat. with hydrogen or oxygen; and L. W. Haase, the effect of light on the oxygen depolarization current of the Fe–Pt couple. N. Harvey observed no luminescent effect during the electrolysis of aminophthalic hydrazide with platinum electrodes.

R. Abegg and co-workers reviewed the work on the e.m.f. of cells with two platinum electrodes with an electrolyte in aq. soln. A. C. Becquerel obtained a difference of potential with a cell Pt | KOH, HNO_3 | Pt; C. Matteucci, with Pt | H_2SO_3(or K_2SO_3), HNO_3(or H_2CrO_4) | Pt; J. Hopkinson, A. Walcker, M. Faraday, and J. Müller studied similar combinations. L. Bleekrode used conc. and dil. soln. of platinic chloride as electrolyte. M. Berthelot, E. Branly, F. P. Dulk and L. Moser, A. van Eccher, F. G. Henrici, M. H. Jacobi, J. P. Joule, S. Pagliani, F. Plzak, J. C. Poggendorff, F. M. Raoult, F. Richarz, A. de la Rive, K. Schreber, and E. Warburg, used other electrolytes. A. C. Becquerel, and G. Quincke, observed a difference of potential with platinum and spongy platinum in conc. nitric acid; C. Fromme with hydrogenized platinum and nitric or chromic acid; C. F. Schönbein, with platinum, and platinum rubbed with a piece of phosphorus; C. E. Fawsit, with polished or hammered platinum, and annealed platinum in a soln. of platinic chloride; J. M. Gaugain, in distilled water with platinum and platinum rubbed with sand-paper, filter-paper, or linen; and A. Bringhenti observed an e.m.f. is developed when a large electrode of platinized platinum and a small one of smooth platinum is placed in an alcoholic soln. of the corresponding sodium alkoxide—methyl, ethyl, or propyl alcohol. The current is not very constant, and varies with the time the circuit is closed, and with the surface of the electrodes. E. du Bois-Reymond, H. Wild, R. Hunt, and F. Zantedeschi observed an e.m.f. is developed when one of two electrodes of the same size is under pressure; and E. du Bois-Reymond, F. G. Henrici, M. Krouchkoll, and E. Becquerel, when the electrolyte about one of the two electrodes is agitated. O. Erbacher studied the exchange of ions on the surface of a platinum electrode; H. Jablczynska-Jedrzejewska, the poisoning of the cathode with hydrogen sulphide; R. Audubert, the inversion potential; and R. G. van Name and F. Fenwick, H. D. Kirschman and co-workers, S. Sekine, A. H. Wright and F. H. Gibson, K. Horovitz, and A. F. Guerasinoff, J. L. R. Morgan and O. M. Lammert, I. I. Schukoff and co-workers, B. Bruns and A. Frumkin, I. M. Kolthoff and T. Kameda, L. P. Hammett, and M. Thalinger and M. Volmer, the use of the platinum electrodes in electrometric titrations. G. S. Forbes and E. P. Bartlett found that some reducing agents, as, for example, ferrous sulphate, arsenious acid, chromous sulphate, and potassium ferrocyanide, increase the oxidizing potential of the dichromate ion on platinum by amounts up to 0·2 volt. No other oxidizing agent has been found to give a similar effect. The potential increases continuously up to the point where all the dichromate is reduced, and then drops suddenly when excess of the added reducing agent is present; and the reaction can be applied to the electrometric titration of a dichromatic soln. with a ferrous salt. A. C. Becquerel observed that an electric current is developed when platinum wires are inserted in fruits and tuberous roots.

W. R. Grove [5] observed that platinum charged with hydrogen as a **gas electrode** in oxygen is positively charged; and E. Becquerel also found it positive in air or condensed oxygen. F. Streintz found that hydrogenized platinum is electronegative towards ordinary platinum; and R. Lorenz and A. Mohn observed that the potential of a hydrogen electrode of 1 atm. press. on platinized platinum in water against a 0·1N-electrode, is 0·75 volt. G. Markovsky found that the e.m.f. of a platinum plate in hydrogen against a platinum plate in gas-free sulphuric acid is 0·646 volt; and when oxygen is substituted for hydrogen, the current is in the opposite direction, and the e.m.f. is 0·372 volt. Electrolytic hydrogen,

and hydrogen from zinc and sulphuric acid, give the same value for the e.m.f.; and a similar result is obtained with electrolytic and chemically prepared oxygen. The e.m.f. of an oxygen cell is diminished by the addition of platinum sulphate to the soln., whilst that of the hydrogen cell increases—the sum of the two remaining constant. The e.m.f. is independent of the density and temp., up to 70°, of the gas. F. Förster observed that the potential communicated by oxygen to platinum is characteristic of a chemical compound—a platinum oxide; and that the e.m.f. of hydrogen towards oxygen between platinized electrodes depends on the electrode material. G. N. Lewis showed that the e.m.f. of the gas cell is less than corresponds with the formation of the water, and hence the value 1·14 volt observed by N. T. M. Wilsmore, V. Czepinsky, and E. Bose at 25° and 1 atm. press. is too high. The subject was discussed by R. Abegg and J. F. Spencer, K. Bennewitz and W. Schieferdecker, S. J. French and L. Kahlenberg, G. Grube and H. Reinharat, F. Haber, R. Köhler, R. Seeliger and M. Reger, and J. B. Westhaver. Gas-cells with platinum electrodes were studied by W. Beetz, R. Höber, J. A. Kendall, L. Mond and C. Langer, H. F. Morley, J. Pieper, Lord Rayleigh, C. F. Schönbein, and M. Thalinger and M. Volmer; and Z. Szabo, and J. J. Hermans, the cell Pt | H_2,m_1HCl | $m_2HCl_2H_2$ | Pt, at 25°.

C. F. Schönbein observed that platinum in water containing ozone, chlorine, bromine, or iodine is electronegative towards platinum in distilled water. F. Schulze-Berge found that platinum saturated with hydrogen is electropositive, and on contact with ozone is electronegative to a platinum plate in air. The potential difference decreases with time, but does not vanish completely. In chlorine, platinum is electropositive to silver. According to R. Luther and J. K. H. Inglis, when the anode liquid of an electrolytic cell contains a strong oxidizer, and a platinum electrode dipping in it is combined with a calomel electrode, the e.m.f. is about 1·1 volts. The oxidizer is supposed to be ozone. Different acids saturated with ozone give under similar conditions, and within narrow limits, the same e.m.f. Electrodes charged with oxygen give a somewhat lower value, whilst a charge of hydrogen raises the oxidation potential. The increase produced by hydrogen soon passes away, and the electrode regains its normal value. The electrode can be freed from either oxygen or hydrogen by a mixture of ferrous or ferric salts. The ozone gas cells were studied by A. Brand, O. Mumm, S. Jahn, and L. Gräfenberg; oxidizing gas cells by C. Fredenhagen; and the Volta effect in water vapour by E. Dubois.

According to W. R. Grove, the sequence of the e.m.ff. of platinum foil charged with different gases, so arranged in the series that platinum charged with a given gas is positive towards platinum charged with one of the preceding gases in the series is: chlorine, bromine, iodine, oxygen, nitric oxide, carbon dioxide, nitrogen, camphor, ethereal oils, ethylene, ether, alcohol, sulphur, phosphorus, carbon monoxide, and hydrogen. B. O. Peirce observed that the nature of the liquid has a great influence on the e.m.f. of any combination of two gases in the gas cell.

At ordinary temp. the relative e.m.f. with water and hydrogen and oxygen is 0·874; nitrous oxide, 0·790; carbon dioxide, 0·981; nitric oxide, 0·933; air, 0·807; water, 0·807; and carbon monoxide, 0·404; with dil. sulphuric acid, and hydrogen and oxygen, 0·926; hydrogen and carbon dioxide, 0·892; and hydrogen and nitric oxide, 0·768; with hydrogen and oxygen and a soln. of sodium sulphate, 0·698; in a soln. of potassium sulphate, 0·698; with a soln. of zinc sulphate, and hydrogen and oxygen, 0·771; hydrogen and carbon dioxide, 0·820; and hydrogen and nitric oxide, 0·860; with water and iodine and bromine, 0·335; with a soln. of sodium bromide, and hydrogen and bromine, 1·252; with a soln. of potassium bromide, and hydrogen and bromine, 1·253; and oxygen and bromine, 0·500; a soln. of potassium iodide, and oxygen and iodine, 0·057, and hydrogen and iodine, 0·861; with dil. hydrochloric acid, and hydrogen and nitric oxide, 0·765; hydrogen and oxygen, 0·855; and hydrogen and chlorine, 1·360; with a soln. of potassium chloride, and hydrogen and chlorine, 1·390; and with a soln. of sodium chloride, and hydrogen and chlorine, 1·390; oxygen, 0·760; carbon dioxide, 0·846; and nitric oxide, 0·750. At a temp. between 75° and 80°, with water, and hydrogen and oxygen, 0·828; nitric oxide, 0·945; carbon dioxide, 0·875; nitrous oxide, 0·780; and water, 0·954.

W. Beetz found the relative e.m.f. in volts of platinum electrodes in different gases to be 3·49 in oxygen against water; 23·98 in hydrogen against oxygen; 20·48 in hydrogen against water; 12·12 in hydrogen against carbon monoxide; 16·37 in carbon monoxide against bromine; 28·32 in hydrogen against bromine; 9·50 in air against chlorine; 30·25 in hydrogen against chlorine; and 20·50 in hydrogen against air; whilst for platinized platinum in the following gases against platinum charged with hydrogen in dil. sulphuric acid, he found the relative values: in chlorine, —46·6; in bromine, —32·3; in oxygen, —16·1; in iodine, —15·8; in nitrous oxide, —5·3; in cyanogen, —5·0; in carbon dioxide, —3·8; in nitric oxide, —2·1; in air, —2·0; in carbon disulphide, 1·7; in methane, 6·7; in phosphorus vapour, 16·1; in carbon monoxide, 28·5; in hydrogen sulphide, 69·0; and in hydrogen, 81·4. Smooth platinum gives nearly the same values. V. Hoeper found the potential of a platinum plate charged with carbon monoxide against a soln. of cuprous chloride in hydrochloric acid to be —0·78 to —0·72 volt.

J. G. Davidson measured the conductivity of a bunsen flame into which a soln. of salt has been injected by measuring the current produced by an e.m.f. of 400 volts. Ionization of the salt occurs only when the platinum cathode coated with salt attains the temp. of the flame. The metal retains the salt in a solid state for a long time. The current increases when the distance between the electrodes is decreased, and varies with the position of the anode. When the anode is coated with the salt instead of the cathode, only about a quarter of the current is obtained. The temp. of the flame or salt practically determines the conductivity of the flame. Numerous ions are formed in the inner cone of a pure flame, but they recombine in the region immediately above. The subject was investigated by F. V. Bossche, R. von Hasslinger, G. Moreau, and E. Wiedemann and H. Ebert.

C. R. A. Wright and C. Thompson observed that an electric current is developed when a thin layer of spongy platinum is simultaneously exposed to the action of air and a soln. of brine. The other electrode is submerged in the liquid. Spongy platinum gives a larger current than does platinum foil. The upper plate absorbs a film of oxygen which uniting with the metal generates an electric current. W. G. Hankel noted that electricity is developed when water is dropped into a platinum dish.

H. Davy [6] placed platinum between electropositive gold and electronegative rhodium in the **electrochemical series** in dil. sulphuric acid; and S. Marianini placed it between tellurium and gold in sea-water acidified with sulphuric acid. The general electronegative character of platinum in various soln. was noted by A. R. Arrot, A. Avogadro and I. Michelotti, A. C. Becquerel, E. Becquerel, M. Faraday, G. F. Fechner, J. M. Gaugain, G. Gore, M. H. Jacobi, L. Kahlenberg, E. Lenz and A. Saweljeff, B. Neumann, J. C. Poggendorff, A. de la Rive, O. Scarpa, C. F. Schönbein, W. Skey, F. Streintz, A. Walcker, and C. R. A. Wright and C. Thompson.

The contact potential of platinum was studied by W. Ende; [7] and the polarity of a platinum cell, by F. Streintz. The **electromotive force** of platinum and **hydrogenized platinum** was studied by J. A. Kendall, and A. Schluigin and A. Frumkin; of platinum against **potassium** amalgam with a soln. of platinic chloride as electrolyte, by J. P. Joule, J. Regnauld, and C. Wheatstone; and with dil. sulphuric acid as electrolyte, by W. Beetz, and J. Goodman. The e.m.f. of platinum against **sodium** at —80° was found by E. Dorn and B. Völlmer to be 3·018 volts; and E. Corminas gave with sodium hydroxide as electrolyte, 3·0 volts; with fuming hydrochloric acid, 3·2 volts; with dil. sulphuric acid (3 : 10), 3·3 volts; sodium nitrate and sulphuric acid (3 : 10), 3·3 volts; conc. soln. of potassium chlorate, 3·5 volts, the same soln. with sulphuric acid (13 : 6), 3·6 volts, and the same soln. with fuming hydrochloric acid (1 : 1), 3·6 volts; conc. soln. of potassium dichromate with sulphuric acid (10 : 3), 3·8 volts; fuming nitric acid, 3·8 volts; conc. soln. of potassium permanganate, 4·0 volts, the same

with sulphuric acid (10 : 3), 4·5 volts, or (55 : 50), 4·5 volts. Observations were made by G. Oesterfeld.

G. Wiedemann,[8] and W. Loewenstein have summarized observations on the e.m.f. of cells of platinum against many elements in various electrolytes. The e.m.f. of platinum against **copper** in various electrolytes was measured by H. E. Armstrong, E. Becquerel, W. Beetz, E. Bichat and R. Blondlot, F. Braun, H. Buff, J. P. Joule, M. Krouchkoll, L. Mond and C. Langer, A. von Oberbeck, S. Pagliani, H. Pellat, J. C. Poggendorff, F. M. Raoult, F. Streintz, D. Tommasi, and C. R. A. Wright and C. Thompson; likewise with **silver,** by E. Bichat and and R. Blondlot, E. Branly, F. Braun, W. Hittorf, J. P. Joule, R. Luther, J. C. Poggendorff, and E. J. Roberts; and **gold,** by E. Becquerel, F. Braun, and F. M. Raoult. O. Erbacher measured the e.m.f. of platinum against **polonium.** G. Gore measured the e.m.f. of platinum against **magnesium** with a soln. of many electrolytes; and of platinum against **zinc** or zinc amalgam with dil. sulphuric acid as in A. Smee's cell was studied by W. Beetz, E. Branly, R. B. Clifton, C. Fromme, G. Guglielmo, J. P. Joule, R. T. Lattey and M. W. Perrin, J. Miesler, L. Mond and C. Langer, F. Paschen, J. H. Paterson, F. Richarz, R. Ruer, F. Todt, C. Wheatstone, M. Straumanis and co-workers, and W. Wolff. B. C. Damien observed that with amalgamated zinc, as the concentration of the sulphuric acid fell from 92 to 30, and 0 per cent., the e.m.f. rose from 1·264 to 1·345 volt, and then fell to 1·083 volt. C. R. A. Wright and C. Thompson observed that with platinum sponge or platinum black, in air, with acid of the concentrations 1 : 10, 1 : 20, and 1 : 40, the respective voltages were 1·750, 1·628, and 1·681; and if some persulphuric acid is present, F. Richarz gave 2·06. Observations with other oxidizing agents were made by R. Ruer, and with zinc sulphate soln. by J. Gubkin, A. von Oberbeck, and C. Hockin and H. A. Taylor. A. Crova studied the effect of temp.; and J. Thomsen, and P. A. Favre, the thermal value of the reaction in the cell.

W. R. Grove's cell is of the type Pt | HNO_3,H_2SO_4 | Zn, and it was studied by W. Beetz, O. Behrend, R. Böttger, E. Branly, H. Buff, R. B. Clifton, C. Fromme, C. A. Grüel, R. Ihle, J. P. Joule, A. König, R. Kohlrausch, J. H. Koosen, J. Miesler, S. F. B. Morse, F. Petruschefsky, J. C. Poggendorff, K. Przibram, and J. Regnauld. The theory of the cell was studied by F. Haber; and the thermal value of the reactions in the cell by J. Thomsen, P. A. Favre, and M. Berthelot. Cells of this type with other electrolytes were studied by W. Beetz, F. Braun, H. Buff, N. J. Callan, R. B. Clifton, A. Crova, B. C. Damien, E. Dorn and B. Völlmer, A. von Eccher, G. Gore, E. F. Herroun, J. P. Joule, J. H. Koosen, M. Kugel, A. P. Laurie, S. Pagliani, F. Paschen, J. C. Poggendorff, A. Righi, H. N. Warren, and C. Wheatstone. Combinations of **cadmium** and platinum with various electrolytes were studied by W. D. Bancroft, F. Braun, G. Gore, A. P. Laurie, L. Mond and C. Langer, A. von Oberbeck, J. C. Poggendorff, and C. R. A. Wright and C. Thompson. Cells with platinum and **mercury** with various electrolytes were studied by W. D. Bancroft, G. J. Burch and V. H. Veley, F. Dolezalek, F. Förster, E. Heyn and O. Bauer, R. Ihle, R. Luther, W. Muthmann and F. Frauenberger, B. Neumann, R. Peters, J. C. Poggendorff, F. Richarz, and C. R. A. Wright and C. Thompson.

E. Branly, and G. Gore studied combinations of platinum with **aluminium** in various electrolytes; A. Bartoli and G. Papasogli, P. Bechtereff, W. E. Case, V. Karpen, A. Naccari and M. Ballati, F. Paschen, and S. P. Thompson, of platinum with **carbon**; F. G. Wick, of platinum with **silicon**; H. E. Armstrong, W. E. Case, A. Mazzucchelli, S. Pagliani, H. Pellat, J. C. Poggendorff, and S. Skinner, of platinum with **tin**; F. Braun, B. C. Damien, W. Hittorf, R. M. Raoult, F. Streintz, and G. Tammann and E. Janckel, of platinum with **lead**; W. Hittorf, and A. Bernoulli, of platinum with **chromium**; J. C. Poggendorff, of platinum with **antimony**; J. C. Poggendorff, and G. J. Burch and V. H. Veley, of platinum with **bismuth**; E. Branly, W. Hittorf, J. P. Joule, J. C. Poggendorff, and L. Schönn, of platinum with **iron**; W. Hittorf, of platinum with **cobalt**; W. Hittorf, and V. O. Krenig

and V. N. Uspenskaya, of platinum with **nickel**; and K. F. San, of platinum and **rhodamine-B**.

A few cases have been examined when molten compounds have been employed as electrolyte: thus, H. Davy [9] employed molten lead oxide with zinc and platinum electrodes; M. Faraday, molten potassium chlorate or nitrate, sodium sulphate or phosphate, lead oxide or iodide, and bismuth oxide with platinum and copper electrodes, and molten silver nitrate or chloride with platinum and iron electrodes. R. Fabinyi and G. Farkas, A. C. Becquerel, T. Andrews, and W. Negbaur employed a number of other combinations. P. Lukirsky and co-workers observed that in the electrolysis of crystals of sodium chloride with a platinum anode, platinic or some lower chloride is formed.

W. Dittenberger and R. Dietz [10] found the **transport number** of platinum in soln. containing 0·0493, 0·0096, and 0·00052 grm. of platinum per c.c., decreases with concentration, being respectively 0·137, 0·113, and 0·075; for soln. of $PtCl_4.H_2O$, or possibly $H_2[PtCl_4(OH)_2]$, W. Hittorf and H. Salkowsky gave 0·146 to 0·126 for the transport number of the anion $\frac{1}{2}PtCl_4O$, and 0·854 to 0·874 for the H_2-cation; and W. Hittorf gave for soln. of sodium chloroplatinate, 0·562 for the $PtCl_6$-anion, and 0·438 for the Na-cation. A. Miolati gave 61·5 for the speed of migration of $\frac{1}{2}[PtCl_4(OH)_2]''$; and P. Walden, 53·4 for $[Pt(CyS)_6]$.

F. Haber gave 10^{-140} to 10^{-150} for the electrolytic **solution pressure** of platinum; and B. Neumann gave 4×10^{-36} atm. F. Glaser also remarked on the high soln. press. of platinum in soln. of potassium cyanide. E. Bose discussed the equilibrium: $Pt_{metal}+Pt^{\cdot\cdot\cdot\cdot}\rightleftharpoons 2Pt^{\cdot\cdot}$, and W. Moldenhauer, the thermal changes in the reaction. H. Herwig found 0·000395 farads arc necessary for the discharge of the condenser cell: Pt | H_2O | Pt. The subject was discussed by J. Billitzer, and S. L. Bigelow.

C. F. Schönbein, and A. Brester observed the formation of hydrogen on a platinum cathode hinders the electrolysis. F. Förster and A. Piguet observed that of all the metals so far investigated the cathode potential of platinized platinum for the discharge of hydrogen is the smallest. W. A. Caspari, and A. Coehn gave 0·09 volt for the **hydrogen overvoltage** on plain platinum cathodes; H. G. Möller, 0·08 volt; A. Thiel and co-workers, and E. Breuning, 0·06 to 0·08 volt; and E. Müller, and W. D. Harkins, 0·01 volt at 12°. For platinized platinum, A. Coehn, and W. A. Caspari gave 0·005 volt; W. D. Harkins, 0·002 volt; E. Müller, 0·01 volt; A. Thiel and E. Breuning, up to 0·0001 volt; and J. Tafel, 0·07 volt with a current of 1 ampère. G. Carrara observed 0·02 to 0·04 volt in N-H_2SO_4 and 0·1 volt in N-KOH, and 0·10 volt in N-H_2SO_4 in methyl alcohol, and 0·05 volt in ethyl alcohol. F. P. Bowden and E. K. Rideal, A. Slygin and co-workers, E. Liebreich and W. Wiederholt, N. Koboseff and N. I. Nekrassoff, I. Zlotowsky, A. L. Ferguson and G. M. Chen, J. A. V. Butler and G. Armstrong, F. T. Chang and H. Wick, A. L. Ferguson and G. M. Chen, A. L. Ferguson and G. Dubpernell, A. Frumkin and A. Schligin, S. Glasstone, W. D. Harkins and H. S. Adams, G. R. Hood and F. C. Krauskoff, V. V. Ipatéeff and co-workers, M. Knobel, E. Liebreich and W. Wiederholt, F. Meunier, T. Onoda, P. P. Porfiroff, P. Sederholm and C. Benedicks, A. Smits, and P. S. Tutundzic studied the subject. F. Kaufler showed that the cathode at which there is an overvoltage of hydrogen must be locally heated more than is the case with no hydrogen overvoltage, and the superior reducing power of the former may be due to the elevated temp. He found that benzophenone and acetophenone were not reduced if no heating current be employed, but it did occur with a heating current. The potential of the heated electrode is rather lower than that of the unheated one. C. Marie studied the effect of the viscosity of the electrolyte on the overvoltage of hydrogen. P. Sederholm and C. Benedicks studied the effect of curvature on the overvoltage; H. T. Beans and L. P. Hammett, the hydrogen electrode; I. Slendyk and P. Herasymenko, the separation of hydrogen from platinum cathodes; and P. Herasymenko and I. Slendyk studied the effect of

traces of ruthenium, rhodium, palladium, and iridium on the hydrogen overvoltage of platinum; and A. Gorodetzkaya and B. Kabanoff, the contact angle of the hydrogen bubbles. N. Thon electrolyzed soln. of platinum salts with an electrode of rare gas. N. Koboseff and N. I. Nekrassoff studied the emission of electrons during the cathode polarization of platinum; M. O. Charmandarian and B. I. Pervuschin, the electrokinetic potential; and R. Köhler, the effect of occluded hydrogen on the reduction potential. C. O. Henke and O. W. Brown observed no relationship between the catalytic activity of metals and their overvoltages; A. Sieverts and P. Luegg, no effect of α-naphthoquinoline on the potential of hydrogen separation on platinum; and J. M. Ort and M. H. Roepke, the effect on soln. of sugar.

A. Coehn and Y. Osaka observed that the **oxygen overvoltage** of a plain platinum anode is very high, for it is 1·67 volts, and that of a platinized platinum anode is 1·47 volts. G. Tammann and F. Runge, P. S. Tutundzic, J. A. V. Butler and co-workers, T. Onoda, S. Glasstone and A. Hickling, A. D. Garrison and J. F. Lilley, H. M. Cassel and E. Krumbein, E. Tommila, and F. Glaser made observations on the subject, and F. Haber reported the formation of some hydrogen dioxide at the anode. F. Förster and A. Piguet found that the rate of increase of the anode potential of platinum in $2N$-KOH, or $2N$-H_2SO_4, is greater than it is with palladium, iridium, iron, and nickel. The subject was studied by V. V. Pitscheta, A. Rius, and F. P. Bowden. The electrolytic valve action was studied by E. Newbery. L. W. Haase observed that the oxygen depolarization current is favoured by darkness. A. P. Rollet, and J. W. Shipley and C. F. Goodeve studied alternating current electrolysis with platinum, copper, and silver electrodes; and V. Cupr, oxidation-reactions at the platinum anode.

L. Arons emphasized the fact that with platinum electrodes it requires a very feeble e.m.f. to develop hydrogen and oxygen in the electrolysis of suitable aq. soln. D. Reichinstein observed that the formation of hydrogen on a platinum cathode proceeds more rapidly than is the case with oxygen on a platinum anode under quite similar conditions. A. Coehn found the reversible production of hydrogen on platinized platinum is 1·08 volt. K. Bennewitz observed that the **decomposition potential** of *sulphuric acid* with rotating platinized electrodes is 1·46 volts. The decomposition at this potential is supposed to occur only at certain points on the electrode, and to become general at a voltage between 1·50 and 1·63. Previous investigators observed breaks at 1·47 and 1·95 volts in the curves representing the variation of the voltage and the change of e.m.f. in the electrolysis of sulphuric acid, but these breaks were not observed with the rotating electrodes. There is a break at 2·20 volts with a soln. of alkali hydrosulphate in conc. sulphuric acid which is supposed to represent the formation of persulphuric acid: $2HSO_4' \rightleftharpoons H_2S_2O_8+2\oplus$. The break at 1·08 volts was observed only with stationary electrodes, and it is connected with the passivity of the metal. There is a break at 0·76 volt with both stationary and rotating electrodes, and it is supposed to be connected with the formation of platinum oxides or hydroxides, and not with passivity. G. Armstrong and co-workers studied the subject. K. Bornemann found that platinum electrodes in N-H_2SO_4 with *hydrogen dioxide* furnish a curve with a break at 1·20 to 1·22 volts, and with electrodes which have been heated to redness, at 1·06 to 1·08 volts. A. Mazzucchelli and C. Barbero also investigated the potential with soln. of hydrogen dioxide; and O. Mumm, and F. Förster, the potential of *ozone* formation. The decomposition voltage curve of *hydrochloric acid* was discussed by E. Müller, R. Luther and F. J. Brislee, and E. Bose. According to G. Pfleiderer, when a dil. soln. of hydrochloric acid is electrolyzed with fresh platinum anodes, and the current is kept constant, the potential rises gradually from 1·4 volts to about 1·9 volts, when oxygen is given off freely. The oxidation of the platinum may be due to the influence of hypochlorous acid formed by the action of chlorine on the water. Both oxygen and chlorine are formed, and the formation of oxygen can be regarded as a secondary phenomenon: $2Cl_2+2H_2O=4ClH+O_2$; and D. Macaluso also studied the behaviour of platinum in a soln.

of chlorine in hydrochloric acid. A. Coehn and Y. Osaka found that with a soln. of *potassium hydroxide*, cooled by a freezing mixture, much ozone is evolved with a platinum anode at 3 volts. W. Kettembeil observed a break in the decomposition curve at 1·32 volts. G. Armstrong and co-workers studied the subject. A. Coehn and St. Jahn studied the phenomenon with soln. sat. with *carbon dioxide*; W. Kettembeil, with soln. of *alkaline earth chlorides*; and B. Kamiensky, the increased negative charge of a platinum electrode in a soln. of potassium chloride in the presence of potassium xanthate.

The deposition potential of copper, silver, gold, zinc, cadmium, and iron on platinum was studied by A. Coehn; of lead dioxide, by K. Elbs and J. Forssell; of nickel, by G. Coffetti and F. Förster; and of platinum, by G. Bodländer, B. Neumann, and J. Wagner. B. Bruzs studied the separation of hydrogen, oxygen, and silver at bright platinum electrodes. G. Grube and co-workers observed that in conc. hydrochloric acid, electrodeposited platinum dissolves anodically more rapidly than rolled sheet. The dissolution of active platinum begins when $E=1$ volt, and chlorine begins to be evolved at the passive pole at 1·2 to 1·4 volts. Platinum can be transferred electrolytically from anode to cathode in M-H_2PtCl_6 in $5N$-HCl at 75°. With low current densities, the platinum dissolves at the anode as $Pt^{\cdot\cdot\cdot\cdot}$, but with high current densities, part dissolves as $Pt^{\cdot\cdot}$. B. Kabanov and A. Frumkin studied the bubble formation on platinum electrodes; M. O. Kharmadaryan and B. I. Pervuschin, moving electrodes; and M. O. Charmandarian and B. J. Pervuschin, N. Thon, K. Gostkowsky, T. Malarsky and K. Gostkowsky, A. Coehn and O. Schafmeister, and S. Procopiu, the electrokinetic potential.

N. Gautherot,[11] and P. Sue observed that if platinum wires which have been used as electrodes in a soln. of salt, be put under and over the tongue, with the wires in contact, the taste alters owing, it was suggested, to the electrolysis of the water. The **polarization** of platinum cathodes in dil. sulphuric acid was observed by A. C. Becquerel, G. Bird, E. du Bois-Reymond, A. Crova, G. T. Fechner, C. Fromme, J. M. Gaugain, J. Harty, H. von Helmholtz, F. C. Henrici, G. Jones and S. M. Christian, M. Krieg, P. L. Maréchaux, E. Pirani, J. C. Poggendorff, F. M. Raoult, C. F. Schönbein, H. Schröder, E. I. Spitalsky and V. V. Picheta, F. Streintz, P. G. Tait, P. S. Tutundzic, E. Warburg, and J. C. von Yelin. M. Berthelot, J. A. V. Butler and G. Armstrong, H. Fricke, A. N. Frumkin and A. Shluigin, C. M. Gordon, W. T. Heys, E. Merritt, N. I. Nekrassoff, A. V. Pamfiloff and O. S. Fedorova, E. Rothé, I. Slendyk, O. Stelling, I. Wolff, and E. E. Zimmerman attributed the cathodic polarization of platinum to the formation of hydrides; and in the case of the anode, E. Rothé attributed the result to the formation of platinum oxides. H. Edler and C. A. Knorr observed that adsorbed hydrogen greatly influences the current-voltage curves of platinum electrodes in benzene. F. Richarz observed that the formation of persulphuric acid, ozone, or hydrogen dioxide exercised no influence on the polarization of platinum in dil. sulphuric acid. The maximum polarization of platinum was found by W. Hallock to be 1·95 volts; E. Pirani gave 2·21 to 2·29 volts; C. Wheatstone, 2·23 volts; J. F. Daniell, 2·49 to 2·857 volts; H. Buff, 2·56 volts; J. C. Poggendorff, 2·33 volts; A. F. Svanberg, 2·31 volts; and F. Richarz, 2·5 volts. The average for dil. sulphuric acid is near 2·8 volts. Observations on the subject were made by A. Wüllner and K. R. Koch, J. L. Kassner and co-workers, C. B. Jolliffe, M. Wien, J. B. Henderson, F. Exner, W. Beetz, N. Nekrassoff, J. Parnell, P. G. Tait, F. Krüger, and F. M. Raoult. V. Karpen studied the polarization in a soln. of potassium iodide and iodine; and W. H. Hunter and L. F. Stone, inorganic depolarizers.

R. Thöldte found the polarization in 10 per cent. sulphuric acid with *feeble strength of current*, is approximately doubled when the strength of the current is doubled, and with currents of greater strength, the increase is smaller, and approaches a constant value. The subject was studied by F. Richarz, H. von Helmholtz, A. W. Witkowsky, A. Bartoli, A. Bartoli and G. Poloni, H. Buff, J. A. Fleming,

J. G. MacGregor, H. Draper, E. Lenz, S. Glasstone and G. D. Reynolds, J. C. Poggendorff, and C. Fromme. With currents of feeble intensity, the polarization on the cathode decreases with *time*, and increases on the anode; with more intense currents, the polarization at the anode soon attains a constant value. The subject was studied by W. Beetz, A. Bernstein, E. Edlund, F. Förster, C. Fredenhagen, J. B. Henderson, K. R. Klein, M. Krieg, D. Macaluso, A. Naccari and G. Guglielmo, J. Parnell, W. Peddie, F. M. Raoult, J. Shields, and F. Streintz. According to H. Draper, the polarization increases about 1 per cent. for a rise of *temperature* of 4°. The subject was investigated by T. R. Robinson, R. Abegg, F. Exner, A. Bartoli, A. de la Rive, W. Beetz, J. C. Poggendorff, and F. M. Raoult. R. Thöldte found that the polarization decreases as the *size of the electrodes* is reduced until it attains a constant value. The subject was studied by A. Bartoli, E. Lenz, W. Andauer, and C. Fromme. The effect of the *concentration of the electrolyte* was examined by E. Bouty, C. Fromme, and J. M. Gaugain; and the rate of the reaction with hydrogen on the cathode, by L. P. Hammett. E. Lenz observed that with the same current density, the polarization decreased with increasing conc. of sulphuric acid; and A. Bartoli, that the addition of glycerol lessened the polarization. The nature of the *surface of the electrodes* was found by J. C. Poggendorff to be such that with smooth platinum electrodes, the maximum polarization was 2·12 to 2·33 volts, and with platinized platinum, 1·83 to 1·85 volts. The subject was studied by C. Fromme, J. Roszkowsky, E. E. Zimmerman, J. Tafel, E. Brunner, and A. Friessner. H. J. T. Ellingham discussed the behaviour of nitric acid at a platinum cathode.

C. F. Schönbein noted that in the electrolysis of water with an anode of smooth platinum and a cathode of platinized platinum gas is developed less vigorously than when the electrodes are reversed. R. Luther noted that with ozone, the oxidation potential with plain electrodes is larger than it is with platinized electrodes. The subject was discussed by F. Förster, and F. Förster and E. Müller. The comparison of the two electrodes in the electrolysis of alkali chloride soln. was made by F. Haber, H. Wohlwill, R. Lorenz and H. Wehrlin, F. Förster and E. Müller, E. Müller, F. Winteler, W. Oechsli, and A. Bültemann; the electro-oxidation of ammonium sulphate was studied by A. Bültemann; the reduction of formaldehyde alkaline soln., by A. Bringhenti; the electrolysis of formic acid, by T. Salzer; the electro-oxidation of potassium ferrocyanide, by A. Brochet and J. Petit.

According to K. R. Koch,[12] the anodic polarization of a platinum electrode in acidulated water by oxygen with an electric current insufficient to produce any perceptible decomposition, is greater than the polarization of the other electrode by hydrogen. E. Cohn observed that the resistance of a voltameter with large platinum plates in dil. acid is scarcely affected by polarization. E. I. Spitalsky and V. V. Pitcheta said that the potential at platinum anodes during the passage of a current depends on the formation of a film of mol. oxygen, or suboxide. When the current is broken, the potential depends on the accumulation of at. oxygen. The behaviour of an anode depends on its previous history, and reproducible results can be obtained only under strictly uniform conditions. The subject was discussed by L. Arons, A. Bartoli, W. Beetz, M. le Blanc, E. du Bois-Reymond, F. P. Bowden, J. A. V. Butler and G. Armstrong, J. Daniel, H. Dufour, F. Exner, C. Fromme, W. L. Hildburgh, T. P. Hoar, H. Luggin, D. Macaluso, C. Matteucci, G. Meissner, T. A. L. du Moncel, J. L. R. Morgan and co-workers, E. Müller, E. Müller and F. Spitzer, W. Nernst and A. M. Scott, K. Ochs, N. Piltschikoff, J. C. Poggendorff, A. de la Rive, V. Rothmund and A. Lessing, E. I. Spitalsky and V. V. Pitcheta, F. Strientz, J. Tafel and B. Emmert, and P. S. Tutundzic. A. V. Pamfiloff studied the anodic polarization with platinum and with platinized platinum electrodes, in the form of a loop of wire, in N- and $0{\cdot}5N$-H_2SO_4 with current densities 0·01 to 0·12 amp. per sq. cm. It was found that with the platinum anode, rotating at 300 to 500 revs. per min., the electrode potential rises quickly in the first 5 mins.,

then more slowly, reaching a maximum in 10 to 20 mins. at a current density of 0·04 to 0·1 amp., and 2½ to 3 hrs. at 0·01 amp. After a short interruption of the polarizing current, a different potential occurs, and, in general, the numerical values obtained are not constant in different experiments, although the general character of the curves is the same. These numerical values depend greatly on the previous treatment of the electrode under observation (action of oxidizing or reducing agents, cathode polarization, etc.). With a platinized electrode the maximum is attained more slowly and the results are more constant; short interruptions of the current have no effect on the electrode potential. The difference between the potential of the platinized and the solid electrode is 0·1 to 0·2 volt, not 0·4 to 0·6 as observed by F. Förster. The results are explained by the interaction of the surface of the electrode with the gas generated in the process of electrolysis, the metal suffering a change from which it recovers only after some time; the question of whether an oxide of platinum or a solid soln. of the gas in platinum is formed is an open one. J. A. V. Butler and G. Drever observed that platinum is anodically polarized in acidic and alkaline soln., and an adsorbed layer of oxygen is formed prior to the establishment of the oxygen overvoltage, but, as in the case of iridium, there is no evidence of a slow formation of oxides of a peroxidic character such as occurs with palladium and rhodium.

The depolarization potentials were found by V. V. Pitcheta to be inversely proportional to the current density for both smooth and platinized platinum. The depolarization of the platinum was studied by J. Billitzer, F. Weigert, and E. Müller. G. Meissner found that platinum is not polarized by oxygen at ordinary temp., but it is polarized at a red-heat; ozone was found by G. Bodländer, and C. F. Schönbein to polarize platinum negatively. F. Kaufler and C. Herzog found that with plain platinum electrodes in the best conducting mixture of sulphuric acid and water, there is contact resistance of about 3 ohms per sq. cm. of electrode surface with a current of 0·01 to 0·02 ampère, this decreases with an increase in the current density. The subject was investigated by J. C. Poggendorff, R. Ruer, O. Troje, W. W. H. Gee and H. Holden, and K. R. Koch and A. Wüllner. A. L. Clark studied the polarization capacity and the electrical double layers; and K. R. Klein studied the rate of anodic depolarization. G. Armstrong and co-workers, and J. A. V. Butler and G. Armstrong observed some periodicities in the anodic polarization of platinum electrodes in dil. sulphuric acid saturated with hydrogen; and A. Günther-Schulze, the effect of platinum salts on valve metals.

According to C. F. Varley,[13] with two platinum plates, 6·45 sq. cm. surface, the polarization capacity, C microfarads, with different e.m.f., E volts, is:

E . .	0·2	0·4	0·8	1·0	1·2	1·4	1·6
C . .	175	210	385	408	467	484	542

The subject was investigated by R. Blondlot, F. Kohlrausch, P. Schönherr, E. Warburg, W. Wien, A. M. Scott, F. Krüger, and A. P. Sokoloff; and the polarization capacity over a wide frequency, by I. Wolff. L. R. Morgan and co-workers studied the reproducibility of quinhydrone electrodes with platinum.

T. Andrews [14] observed that the contact of platinum with bismuth makes the bismuth passive; W. Heldt obtained a similar result with tin; L. Schönn, with iron; and P. Monnartz, with ferrochromium alloys. The surface of anodically polarized platinum, and the surface of platinum which has been treated with strong oxidizing agents, were found by F. Haber to be changed, for the metal will then liberate iodine from a soln. of potassium iodide. The platinum anode saturated with oxygen is not completely reversible. From potential measurements also, it is assumed that the insolubility of platinum is a form of **passivity** produced by the formation of a superficial layer of oxide on the metal. The film of oxide is electrically active, but has a smaller oxygen press. than the gas itself. The passivity of platinum was discussed by G. Grube, R. Ruer, V. V. Picheta, W. J. Müller and O. Hering, G. C. Schmidt, E. Grave, F. Förster and J. Yamaski, J. Steiner and

L. Kahlenberg, E. S. Hedges and J. E. Myers, A. Günther-Schulze, G. Tammann, M. Thalinger and M. Volmer, K. Bennewitz, and G. Senter. E. Müller observed that in an electrolytic cell containing hydrochloric acid, a gradually increasing anodic potential difference results in the current strength rising to a constant value which is maintained for an interval—Fig. 16. It was assumed that the ion in soln. primarily concerned in the electrolysis is exhausted in the region corresponding with the flat part of the wire. R. Luther and F. J. Brislee showed that this explanation cannot be correct, and they suggest that here Cl_2''-ions are present in the soln. and that these ions are in equilibrium with the Cl'-ions, and the exhaustion of these ions is responsible for the constant value of the current strength. The condition of the platinum anode is the most important factor. When the anodic potential difference, after a gradual increase, is gradually diminished, without break of current, the corresponding variation of the current strength is not always that given by the first potential difference-current curve. The current strength may fall away rapidly almost to zero, the electrode having become "passive." If, while the electrode is still passive, the potential difference is again increased, the horizontal portion of the potential difference-current curve cannot now be obtained. This passive condition is due to a superficial change of the platinum anode, and has nothing to do with the solution. It disappears immediately if the current is broken, and if the anode potential difference is allowed to fall below 1·6 volts, a passive electrode becomes spontaneously active. Further, if the change of potential difference is reversed before $i_{\text{lim.}}$ is reached, the passive condition does not set in. There are thus three states of the platinum surface. The production of the passive condition does not depend on the presence of Cl'-ions, but begins in acid solutions at about 1·9 volts and vanishes at about 1·6 volts.

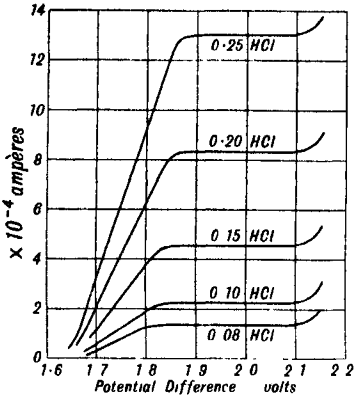

Fig. 16.—Anodic Potential—Current Curves of Hydrochloric Acid.

C. Fredenhagen observed that platinum electrodes in alkaline soln. of mixtures of potassium ferrocyanide and ferricyanide are non-polarizable; and C. Grube, that in the electrolytic oxidation of a ferrocyanide in neutral or alkaline soln., the reaction $FeCy_6'''' = FeCy_6''' + \ominus$ is probably instantaneous. Passivity may be produced by a thin film of oxide on the metal, or by adsorbed oxygen, dependent on the conditions. G. Just also found that the accelerating action of platinum on the reaction between potassium ferricyanide and iodide is connected with the oxidation and reduction of the metal. The anodic formation of a brown film of oxide on platinum was observed by W. Beetz, and the subject was studied by R. Ruer, S. Popoff and M. J. McHenry, W. Nernst and H. von Wartenberg, F. Haber and L. Bruner, G. Pfleiderer, F. C. Frary, G. C. Schmidt, M. le Blanc, K. R. Koch, M. Krouchkoll, K. Waitz, H. Hauser, R. Lorenz and co-workers, F. Förster, C. Marie, L. Wöhler, L. Wöhler and F. Martin, L. Arons, G. Grube, L. Cailletet and E. Collardeau, M. Berthelot, and H. N. Warren. According to C. Marie, the brown colour observed by F. Kohlrausch on the anode during the electrolysis of soln. of platinum chloride is due to a superficial oxidation of the platinum; and similarly with the electrolysis of soln. of sodium hydroxide, nitric acid, or hydrochloric acid with platinum electrodes. E. P. Schoch showed that the observed anodic potential of platinum is not usually the reversible potential of the oxygen, but rather of a platinum oxide; and C. M. Gordon and F. E. Clark, that the capacity of a platinum electrode is conditioned by a film of oxide. G. Lippmann said that the discharge of hydrogen or oxygen from a platinum plate in electrolysis does not

affect the optical properties of the electrodes. A. Rundspaden, and W. Hampe observed no oxidation of platinum at the anode during electrolysis. J. L. R. Morgan and O. M. Lammert studied the quinhydrone electrode with platinum and platinum alloys.

According to F. Haber,[15] a platinum electrode in a soln. of potassium hydroxide gradually acquires a film of finely-divided platinum ; the electrode becomes rough and dull in hydrochloric acid ; and it acquires a film of platinum-black in hypochlorite soln. The subject was discussed by G. Bredig and F. Haber, M. Sack, and A. P. Sokoloff. F. Giordani and B. Focaccia, and P. Schoop found that with soln. of calcium chloride the electrode acquires cracks and pores, but when the platinum is alloyed with 10 per cent. of iridium, the metal is stable. R. Ruer observed the disintegrations of platinum electrodes in the electrolysis of nitric acid by an alternating current, owing to the alternate oxidation and reduction of the metal. The subject was discussed by P. Burger. W. D. Bancroft and J. E. Magoffin studied the energy changes in the electrolysis of sulphuric acid.

The attack of platinum anodes in the direct current electrolysis of dil. sulphuric acid was observed by K. Arndt,[16] G. Grube and co-workers, A. Brochet and J. Petit, M. Margules, J. Tafel and B. Emmert, and G. Senter ; hydrochloric acid, and soln. of chlorides, by W. H. Wahl, F. Haber, F. Bran, H. C. P. Weber, C. Marie, E. H. Archibald, M. Margules, F. Schulz, and A. Nobis ; ammonia, ammonium salts, and potash lye, by E. Reichel ; ammoniacal nitrate soln., by A. Thiel ; nitric acid, by M. Margules ; soln. of sulphides, by W. Schulte, F. W. Durkee, W. Klapproth, and H. Ost and W. Klapproth ; soln. of cyanides, by T. Wilm, F. Reichel, A. Fischer, L. Elsner, R. Ruer, F. Glaser, A. Brochet and J. Petit, and F. M. Perkin ; soln. of ammonium acetate and chrome-alum, by C. Engels ; phosphoric acid, formic acid, and acetic acids, but not oxalic acid, by M. Margules ; and alkali hydroxides, by G. Janeczek, M. Margules, P. Bechtereff, and E. A. Bourgoin ; molten potassium nitrate, by W. Hittorf ; molten potassium carbonate, by T. Gross ; molten lead chloride, by M. Faraday ; and molten potassium uranium hexachloride, by J. Aloy. The attack of platinum electrodes in the alternating current electrolysis of dil. sulphuric acid was studied by R. Ruer, A. Brochet and J. Petit, M. Margules, and W. J. Müller ; in hydrochloric acid, by P. Burger, and M. Margules ; in nitric acid, by H. J. T. Ellingham, M. Margules, and P. Burger ; in soln. of alkali hydroxides, by M. Margules ; in sodium phosphate soln., and phosphoric acid, by M. Margules, and E. Drechsel ; in soln. of sulphides, by F. W. Durkee ; and in soln. of ammonium carbonate and carbamate, by E. Drechsel, and B. Gerdes ; and A. Brochet and J. Petit, in soln. of cyanides.

The electrolysis of sulphuric acid by alternating currents with platinum electrodes, was studied by P. Burger, F. Krüger, and D. Reichinstein ; and of nitric acid, by T. Gross, and H. Danneel ; and the polarization of electrodes with alternating currents, by S. Glasstone, and N. Isgarischeff and S. Berkmann. Rotating platinum electrodes were used by F. Fischer and co-workers in the preparation of ozone.

Platinum electrodes were used in the formation of ammonia by E. Briner and E. Mettler ; in the electrolysis of ammonium salt soln., by E. Drechsel ; potassium iodide soln., by N. Peskoff and B. Saprometoff ; sodium sulphide soln., by P. P. Lebedew ; in the preparation of nitrogen chloride, by F. Mareck ; in the formation of periodates, by E. Müller ; and in the electrolysis of ferrocyanide soln., by K. Schaum and R. von der Linde, and in the electrolysis of glycerol, and phenol, by A. Bartoli and G. Papasogli. W. Jäger, and K. Kahle tried amalgamated platinum electrodes in place of mercury in the standard calomel cell. Platinum cathodes were employed by A. Brochet, H. Danneel, and K. Bennewitz in the electrolysis of sulphuric acid ; by A. L. Voege, E. Müller, and J. Tafel, in the electrolysis of nitric acid ; by H. Davy, in the electrolysis of phosphoric acid when platinum phosphide is formed ; by W. Thomson, and A. C. Chapman and H. D Law, in the electrolysis of arsenious or arsenic acid when platinum arsenide

is formed; by A. Brester, in the electrolysis of soln. of sodium sulphate when a sodium-platinum alloy is formed; by R. Luther, A. Brochet and C. L. Barillet, W. J. Müller and J. Königsberger, H. E. Medway, and W. S. Kimley, in the electrolysis of soln. of copper salts; by A. Matthiessen, in the electrolysis of a soln. of barium chloride, when a barium-platinum alloy is formed; by A. Millot, W. Peddie, and A. Mascazzini and G. Parodi, in the electrolysis of soln. of zinc salts; by V. Borelli, and R. Abegg, in the electrolysis of mercury salts whereby the platinum is amalgamated; and by J. Miesler, and F. Mylius and O. Fromm, the electrolysis of soln. of platinum chloride—in the latter case no floating metallic films were formed about the cathode. Platinum cathodes were used by W. Löb, and W. Löb and R. W. Moore in the reduction of nitrobenzene; by H. Hofer and F. Jacob, in the reduction of polynitrobodies; and J. Tafel, in the unsuccessful reduction of caffeine. Platinum anodes were employed by H. A. Wilson, in the electrolysis of nitric acid; by A. Bültemann, in that of alkaline soln. of potassium nitrite; F. W. Durkee, sodium sulphide; F. Förster and A. Friessner, A. Friessner, and A. Bültemann, sodium sulphite; and J. B. Westhaver, sulphuric acid; M. G. Levi and M. Voghera used platinum anodes in preparing hyposulphites; E. Müller, F. Richarz, K. Elbs, A. Bültemann, and O. Schönherr, persulphates; and F. Förster and A. Friessner, dithionates. Use of platinum anodes in the electrolysis of soln. of chlorides in the formation of chlorates, and perchlorates was studied by F. Förster and E. Müller, A. Bültemann, F. A. Gooch and F. L. Gates, W. Oechsli, and R. von Hasslinger; the electrolysis of soln. of sodium bromide, by G. Kretzschmar, A. Bültemann, and F. Boericke; and of iodides in the formation of periodates, by E. Müller, and E. Müller and O. Friedberger; in the oxidation of ferrocyanides, by A. Brochet and J. Petit; in the electrolysis of alkaline soln. of formates, and of formic acid, by A. Bültemann, and T. Salzer; alkaline soln. of oxalates and of oxalic acid, by A. Bültemann; of fatty acids, by K. Elbs and O. Brunner; and of sugar soln. by P. Rabe and C. Roy. E. Beutel and A. Kutzelnigg obtained sulphide films by the electrolysis of thiosulphate soln.

The **electrodeposition** of platinum from soln. of hydrochloroplatinic acid was studied by A. C. and E. Becquerel,[17] and C. Luckow, and they did not obtain smooth deposits of the metal. E. G. Weischede found the **deposition potential** from 0·04N-soln. in ammoniacal soln. is —0·57 to —0·53 volt at 20° and current density 10^{-3} amp. per sq. cm.; and in acidic soln. of 20·4 mgrms. of platinum per 100 c.c., at 20° and 60°, respectively, 0·68 to 0·53 volt and 0·69 to 0·59 volt and current density 8×10^{-4} amp. per sq. cm. C. W. Keitel used a bath of a 10 per cent. soln. of ammonium sulphate or nitrate with 5 per cent. free ammonia, and 2 per cent. of platinous diamminonitrite, replenishing the ammonia and nitrate as required. The bath is operated at 95°, with 2·2 volts. C. W. Keitel and H. E. Zschiegner used a bath prepared by boiling platinous chloride with sodium nitrite until the soln. is yellow or colourless, and then adding an excess of ammonia. T. Erdey-Gruz and H. Wick, and C. Marie and N. Thon made observations on the subject. F. Kohlrausch found that chlorine is given off at the anode, and both hydrogen and platinum appear at the cathode. It is, however, doubtful if platinum is the primary product of the electrolysis. An aq. soln. of platinic chloride gave on electrolysis with weak currents, hydrogen alone at the cathode, no platinum separating, and at the anode oxygen was obtained. With stronger currents, a deposit of platinum appears on the cathode and oxygen at the anode. The author regards the depositions of platinum in the last case as due to secondary action, and suggests that platinic chloride exists in solution as H_2PtCl_4O, with the ions H_2 and $PtCl_4O$. The secondary deposition of platinum may be due to the reaction $2H_2+3H_2PtCl_4O=Pt+2H_2PtCl_6+3H_2O$ as the solution gradually changes to one of hydrogen platinochloride. The platinum cathode becomes bent during the passage of the current, perhaps owing to occlusion of the hydrogen taking place with contraction in volume. G. Grube and co-workers observed fine-grained deposits of platinum are produced when a soln. of 0·1M-H_2PtCl_2 in 5N-HCl is electrolyzed at 60° with a current density of 0·01 to 0·02 amp.

per sq. cm., and the current yield is 60 to 70 per cent. At the anode, dissolution of platinum begins at $E=1$ volt; chlorine begins to be evolved at 1·2 to 1·4 volts. W. Hittorf said that the platinum deposited electrolytically from a soln. of alkali chloroplatinate is produced at the cathode by the reducing action of the alkali metal. Observations were also made by W. Halberstadt, H. Danneel, A. Classen, P. K. Frölich and G. L. Clark, E. R. Thews and R. W. Harbison, A. R. Powell and co-workers, E. F. Smith, E. F. Smith and H. F. Keller, L. Schucht, F. Wöhler, A. Joly and E. Leidié, J. W. Langness, P. Haas, C. W. Keitel and H. E. Zschiegner, S. Popoff and A. H. Kunz, D. McDonald, F. Braun, and A. Coehn. E. Liebreich found that in depositing platinum on silver in a soln. of nickel sulphate, platinum shows a slight reaction just prior to the evolution of hydrogen.

A. C. and E. Becquerel found a difficulty in obtaining a smooth deposit, but by using a dil. soln. of the chloride acidified with sulphuric acid, F. Rüdorff, and H. Freudenberg obtained a dull deposit which could be polished with sand. A. Classen employed a hot soln. of the chloride acidified with sulphuric or hydrochloric acid, or mixed with ammonium or potassium oxalate; C. Luckow used a dil. soln. of platinic chloride mixed with sodium chloride; W. Halberstadt, a warm soln. of platinic bromide acidified with hydrobromic acid; and E. F. Smith used a soln. of ammonium chloroplatinate mixed with some sodium phosphate, and phosphoric acid. A. Fischer did not obtain a deposit by the electrolysis of a soln. of potassium cyanoplatinate.

The electrodeposition of platinum on metals has been effected by W. H. Wahl by means of a bath of alkali platinate—a soln. of hydrated platinum dioxide in alkali lye. R. Böttger, J. Wiess, and W. Rathenau employed a bath of alkali chloroplatinate—a soln. of potassium chloroplatinate in alkali lye. M. Roseleur and M. Lanaux, R. Böttger, W. A. Thoms, S. P. Thompson, M. Baum, K. Sadakata, T. Yoshida, and the Platinum Plating Co. used a bath of alkali phosphatoplatinate —say G. Nikolaus' recipe: where the electrolyte is a boiling soln. of 4 grms. of platinic chloride, 20 grms. of ammonium phosphate; 90 grms. of sodium phosphate; and 5 grms. of sodium chloride per litre. The article to be plated should be kept in motion, and a potential difference of 6 to 8 volts employed. P. Jewreinoff, and W. H. Wahl employed a bath of alkali oxalatoplatinate; T. Wilm, F. Glaser, A. Fischer, and H. Freudenberg employed a bath containing cyanide soln.; and R. Böttger, and W. C. Arzen, a soln. of ammonium chloroplatinate and sodium citrate. The subject was discussed by M. Baum, R. Böttger, A. Church, D. Clerk and C. A. Fawsitt, J. B. A. Dodé, H. Elkington, L. l'Hôte, T. Howse, J. H. Johnson, H. H. Lake, W. A. Lampadius, H. H. Landois, S. T. Leo and T. N. Shen, L. B. G. de Morveau, R. Namais, A. Polain, A. E. W. Smith, C. Stahlschmidt, L. M. Stoffel, J. B. Thompson, A. Wogrinz, and J. Langness. M. de Kay Thompson, and C. W. Keitel recommended a mixture of the cis- and trans-forms of platinum dinitritodiamminonitrite obtained by treating a soln. of sodium chloroplatinate with sodium nitrite, boiling, adding a slight excess of ammonia, and dissolving the precipitate, after filtering and washing, in more ammonia. The bath is made up by dissolving 100 grms. of ammonium nitrate or sulphate in a litre of distilled water containing 5 per cent. of ammonia, adding 20 grms. of the solid plating salt, and heating. It is worked at 95° and is quite stable. It is kept ammoniacal, and more salt is added as is necessary. H. S. Booth and M. Merlub-Sobel deposited platinum from soln. of salts in liquid ammonia. R. H. Atkinson studied the electrolytic transfer of the metal using fused chlorides as electrolytes; G. Grube and co-workers discussed the subject. In the electrolysis of soln. of platinum chloride containing cerous chloride, A. B. Schiötz found that platinum alone is deposited. M. Prasad and N. B. Choksey studied the effect of a magnetic field. C. Sandonnini and V. N. Borghello observed no action occurred on electrolyzing carbon tetrachloride with 10 per cent. sulphuric acid and a platinum anode, but with a lead anode dehalogenization occurred.

J. Plücker [18] noted the **spluttering of platinum** from the cathode in a discharge

tube; and G. Granquist found that at 0·6 mm. press., platinum splutters more easily than gold. The loss in weight is independent of the temp. W. Crookes observed that the loss in weight from an electrode weighing 10·1940 grms. was 2·0370 grms. in 24 hrs.; F. Ehrenhaft said that the radius of the spluttered particles is 4.4×10^{-6} to 14.7×10^{-6} cm. With a pressure approximating 0·4 mm., and a current of 0·0006 amp., and voltage E, L. Holborn and L. Austin found the losses in weight in 30 mins., under comparable conditions, to be:

	Air				Hydrogen			
E	890	1190	1300	1440	1280	1430	1890	2090
Loss	0·63	1·04	1·29	1·38	0·54	0·82	0·83	0·74 mgrm.

V. Kohlschütter and R. Müller observed that with a current continuing for t minutes, with a press. p mm., the losses in mgrms. from a 0·5 mm. thick platinum cathode, were:

	Hydrogen	Helium	Nitrogen			Oxygen			Argon	
t	30	30	30	45	70	30	30	40	30	30
p	0·61	0·34	0·55	1·33	0·17	0·24	0·53	0·60	0·70	0·79
Loss	0·9	0·5	2·0	2·6	1·0	1·4	2·4	3·7	0·9	0·8

V. Kohlschütter and T. Goldschmidt, and T. Goldschmidt found that with different gases, the losses of platinum by spluttering were relatively, helium, 0·23; nitrogen, 1·2; oxygen, 1·9; and argon, 5. E. Blechschmidt, R. Blondlot, C. H. Cartwright, W. T. Cooke, R. K. Cowsik, J. Elster and H. Geitel, F. Fischer and O. Hähnel, O. Hähnel, W. Hittorf, E. O. Hulburt, L. R. Ingersoll and L. O. Sordahl, H. Kayser, J. de Kowalsky and E. Banasinsky, E. Marx, K. Meyer and A. G. Schulze, J. Mooser, F. H. Newman, G. Reboul and E. G. de Bollemont, and F. Wächter studied the subject—*vide supra*, the forms of platinum. A. Voet investigated the anodic dispersion; P. Jolibois, the structure of the spark striking the surface of a solution; T. Kinbara observed the effect of a current from a platinum pole on a photographic dry plate.

The fall of potential with a platinum cathode with the **glow discharge** was found by E. Warburg[19] to be 300 volts in hydrogen, and 232 volts in nitrogen free from oxygen; by R. J. Strutt, 226 volts in helium, and 167 volts in argon; R. Defregger, in helium, 168 volts with platinized platinum, and 160 volts with smooth platinum; by H. Dember, 165 volts in helium with a highly polished platinum wire, and 163 volts in argon; by J. W. Capstick, 369 volts in oxygen; and by G. Bode, 320 to 340 volts in chlorine; 376 to 414 volts in bromine; and 380 to 430 volts in iodine. Observations were made by H. Rohmann, O. Klemperer, C. A. Skinner, W. Matthies, F. Müller, O. W. Richardson, H. P. Waran, F. Deininger, and J. A. Cunningham. C. del Rosario investigated the low press. discharge. F. W. Aston discussed the effect of platinum on Crookes' dark space; L. Tonks, anchoring the cathode spot; and A. Janitzky, the effect o, occluded gas in the anode.

According to W. R. Grove,[20] after silver and gold, the **arc discharge** of platinum furnishes the shortest and darkest arc-light of all the metals tried. E. Leccher found that between horizontal platinum electrodes, 5 mm. in diameter, and 2 mm. apart, the difference of potential is 35 volts. L. Arons gave 30 volts for a current of 4·5 amps. in nitrogen at atm. press. with the electrodes 1·5 mm. apart. V. L. Chrisler studied the platinum arc in air; A. J. Dempster, the emission of positive ions; and S. Virtel, the properties of particles from the electric arc. Observations were made by C. E. Guye and co-workers, W. B. Nottingham, H. W. Malcom and H. T. Simon, H. E. Ives, and J. Stark. According to A. Simek and H. Kadlcova, drops of molten tellurium dioxide move from the negative to the positive pole on the surface of hot platinum.

T. J. Seebeck[21] represented platinum in the **thermoelectric series** between palladium and rhodium, and J. P. Emmet observed that a current flows from warm

platinum to the cold metal when in contact with antimony, arsenic, platinum, copper, silver, lead, tin, zinc, mercury, iron, nickel, gold, and bismuth. Observations on the subject were made by J. Cumming, W. G. Hankel, P. O. C. Vorsselmann-de-Heer, H. Rohmann, W. Rollmann, A. Abt, J. M. Gaugain, N. F. Mott, and A. Matthiessen. H. le Chatelier observed that with purified platinum, its position in the thermoelectric scale is not altered by annealing. N. A. Hesehus studied the subject. Observations on the sensitiveness of thermocouples were made by K. E. F. Schmidt; the neutral points were discussed by Lord Kelvin, P. G. Tait, C. G. Knott and co-workers, and M. Chassagny and H. Abraham. C. Benedicks and C. W. Borgmann studied the influence of gas ions on the electrothermal effect; and A. V. Makaroff and I. V. Plastinin, the thermoelectric homogeneity of platinum wires.

A. C. Becquerel observed a **thermoelectric force** with a thermocouple of platinum wires in contact whereby a current flows from the hot to the cold wire; G. Magnus, A. C. Becquerel, B. L. Rosing, J. M. Gaugain, F. C. Henrici, P. Raethjen, and W. Durham observed a thermoelectric force with wires of different structure, *e.g.* hard and soft wires. F. P. le Roux, and E. Cohn observed that with a stretched and an unstretched wire, a current flows through the hot junction from the stretched to the unstretched wire—Lord Kelvin added that this occurs only if the stretching is permanent; and E. Wagner found that a compressed wire gives a thermoelectric force against an uncompressed wire, amounting at 58°, and a press. of a kgrm. per sq. cm., to $0{\cdot}0_{10}186$ volt per degree. P. W. Bridgman observed that the thermoelectric force, $E\times10^6$ volts, with a couple of platinum uncompressed and compressed at p kgrms. per sq. cm.:

	p	10°	20°	40°	60°	80°	100°
$E\times10^6$	2,000	0·30	0·63	1·40	2·23	2·98	3·60
	6,000	0·91	1·96	4·28	6·61	8·76	10·70
	12,000	1·79	3·88	8·60	13·39	17·76	21·57

and the results with one sample of purified platinum against lead were $E\times10^6=-3{\cdot}092\theta-0{\cdot}01334\theta^2$ volts; and with another specimen, $E\times10^6=-1{\cdot}788\theta-0{\cdot}0173\theta^2+0{\cdot}0_4 42\theta^3$ volts. K. Tsuruta studied the effect of longitudinal tension; G. Tammann, and G. Tammann and G. Bandel, the effect of cold work. V. B. Lewes observed that molten platinum heated in the oxy-hydrogen flame gives a greater thermoelectric current than does the molten metal near the m.p. C. G. Knott, and J. Monckman observed that a thermoelectric current flows through the hot junction from non-hydrogenized to hydrogenized platinum. W. Ende, and G. Meyer studied the effect of striction; and J. L. Hoorweg, the effect of different kinds of platinum. J. Würschmidt, and G. K. Burgess and P. D. Sale determined the purity of the platinum by determinations of its thermoelectric force. R. M. Holmes measured the thermoelectric force of these couples. F. Jenkin observed a thermoelectric current between platinum and platinum covered with copper oxide; and R. Bunsen, with platinum and pyrolusite, or platinum and copper pyrites.

E. Heiber measured the thermoelectric force of platinum against the solid *alkali metals*—Li, Na, K, Rb, and Cs. H. C. Barker found that for a temp. difference of $\theta°$, the thermoelectric force, E microvolts, of the *platinum-potassium* couple is:

θ	89·50°	70·86°	50·84°	40·24°	28·64°	17·70°	6·82°
E	840	670	480	380	370	170	70 microvolts

or −0·94 millivolt at 100°. Observations were also made by A. Naccari and M. Bellati. H. C. Barker gave for the *platinum-sodium* couple −0·21 millivolt at 100°, or

θ	84·24°	73·60°	63·46°	52·79°	41·51°	32·16°	12·64°
E	170	150	130	110	90	70	30 microvolts

A. Abt, A. C. Becquerel, J. W. Draper, E. Edlund, J. Galibourg, J. M. Gaugain, A. Hiel, W. Jäger and H. Diesselhorst, I. Klemencic and P. Czermac, G. G. de Metz,

J. Monheim, H. V. Regnault, E. Wagner, and R. von Wegner made observations on the *platinum-copper* couple. A. E. Caswell found 2·29 millivolts between 0° and 36°; E. Wagner, 7·9 millivolts at 60°; M. Chassagny and H. Abraham, —0·0005917 volt between 0° and 100°; and E. Becquerel, 0·000378 volt. W. Jäger and H. Diesselhorst gave for the thermoelectric force at 100°, 0·72 millivolt; J. Dewar and J. A. Fleming, 0·76; K. Noll, 0·73; W. H. Steele, 0·76; and E. Wagner, 0·75 millivolt. K. Noll observed with one junction at 0°:

	57 0°	100°	137°	216·75°
E.m.f.	380·1	731·55	1081·8	1954·6 millivolts

Lord Kelvin gave 64° for the neutral point. K. Bädeker gave 480 millivolts between 0° and 100° for the platinum and cuprous oxide couple. The thermoelectric force of the *platinum-silver* couple was investigated by R. von D. Wegner, G. G. de Metz, A. C. Becquerel, G. Borelius and co-workers, A. Matthiessen, J. W. Draper, and W. Broniewsky. L. Holborn and A. L. Day gave for the thermoelectric force at 100°, 0·72 millivolt; W. Jäger and H. Diesselhorst, 0·71; J. Dewar and J. A. Fleming, 0·78; K. Noll, 0·67; W. H. Steele, 0·73; and E. Wagner, 0·76 millivolt. G. Borelius and co-workers studied the effect against a *silver-gold alloy* at a low temp. L. Holborn and A. L. Day gave for the e.m.f. $E=5{\cdot}891\theta+0{\cdot}132\theta^2$ volts; they also gave for the temp. coeff. 0·00405 volt between 0° and 950°. L. Holborn and A. L. Day gave for the thermoelectric force at 100°, 0·74 millivolt; W. Jäger and H. Diesselhorst, 0·72; J. Dewar and J. A. Fleming, 0·56; K. Noll, 0·71; W. H. Steele, 0·74; and E. Wagner, 0·78 millivolt. Observations were made by A. C. Becquerel. Lord Kelvin gave —3·06 for the neutral point. L. Holborn and A. L. Day also gave:

	900°	700°	500°	300°	200°	100°	−80°	−185°
E . .	16·0	10·6	6·2	3·0	1·7	+0·72	−0·30	−0·16 millivolt

and for the *platinum-gold* couple, $E=-398+8{\cdot}769\theta+0{\cdot}008446\theta^2$ volts between 0° and 1050°, when the temp. coeff. is 0·00389. Observations were made by O. Knopp, and G. G. de Metz. Lord Kelvin gave —1·5° for the neutral point. L. Holborn and A. L. Day, and R. von D. Wegner also gave for the gold-platinum couple:

	1000°	800°	600°	400°	200°	100°	−80°	−185°
E . .	16·8	12·0	7·9	4·5	1·8	+0·74	−0·31	−0·15 millivolt

J. Dewar and J. A. Fleming found that the thermoelectric force of the *platinum-magnesium* couple at 100° is 0·42 millivolt; K. Noll gave 0·40; and E. Wagner, 0·43 millivolt. Observations were made by A. V. Tidblom. W. Jäger and H. Diesselhorst gave 0·75 millivolt for the thermoelectric force of the *platinum-zinc* couple at 100°; J. Dewar and J. A. Fleming, 0·77; K. Noll, 0·74; W. H. Steele, 0·60; and E. Wagner, 0·79. Observations on zinc were made by G. G. de Metz, A. V. Tidblom, and A. C. Becquerel; and on brass, by A. Abt, and G. G. de Metz. Lord Kelvin gave 38° for the neutral point with brass. W. Jäger and H. Diesselhorst gave 0·85 millivolt for the thermoelectric force of the *platinum-cadmium* couple at 100°; J. Dewar and J. A. Fleming, 0·92; K. Noll, 0·88; W. H. Steele, 0·90; and E. Wagner, 0·92 millivolt. Observations were made by A. V. Tidblom. Lord Kelvin gave —12·2° for the neutral point. The thermoelectric force of the *platinum-mercury* couple was found by H. C. Barker to be:

	84·42°	58·56°	39·31°	29 69°	10·64°
E.m.f.	50	40	30	20	10 microvolts

or —0·07 millivolt at 100°. K. Noll gave zero at 100°; and E. Wagner, 0·04 millivolt. Observations were made by C. Matteucci, and P. O. C. Vorsselmann-de-Heer. H. Hörig observed 10^{-6} volt per degree at 150°, and when under a press. of 1400 kgrms. per sq. cm., $2{\cdot}18\times10^{-6}$ volt per degree per kgrm. per sq. cm. W. Jäger and H. Diesselhorst gave 0·38 millivolt at 100° for the thermoelectric force of the *platinum-aluminium* couple; J. Dewar and J. A. Fleming gave 0·40;

K. Noll, 0·37 ; W. H. Steele, 0·38 ; and E. Wagner, 0·41 millivolt. Observations were made by G. G. de Metz. J. Buchanan gave for the thermoelectric force of the *platinum-carbon* couple $E=566+3\cdot94\theta$ microvolts, with the neutral point at $-145°$. J. W. Draper, A. V. Tidblom, and A. C. Becquerel measured the thermoelectric force of the *platinum-tin* couple, and W. Jäger and H. Diesselhorst gave 0·42 millivolt at 100° ; J. Dewar and J. A. Fleming, 0·45 ; K. Noll, 0·40 ; W. H. Steele, 0·41 ; and E. Wagner, 0·44 millivolt. Lord Kelvin gave 44° for the neutral point. A. V. Tidblom measured the thermoelectric force of some tin-zinc alloys against platinum. For the *platinum-lead* couple, W. Jäger and H. Diesselhorst gave 0·41 millivolt ; J. Dewar and J. A. Fleming, 0·44 millivolt ; K. Noll, 0·41 ; and E. Wagner, 0·46 millivolt. J. Buchanan gave $-85°$ for the neutral point ; and M. Avanarius gave $E=0\cdot085(\theta_1-\theta_2)+0\cdot0046(\theta_1-\theta_2)^2$. Lord Kelvin gave 36° for the neutral point. Observations on lead were also made by P. G. Tait, G. G. de Metz, E. Becquerel, and A. V. Tidblom, and on some lead-zinc and lead-tin alloys by A. V. Tidblom, J. Dewar and J. A. Fleming gave for lead for temp. between $\theta°$ and $\theta°$, in c.g.s. units ;

θ .	99·9°	33·2°	11·6°	+21·9°	−90·2°	−135·1°	−181°	−205·6°
E .	−29,630	−6,830	−2,080	+2,800	−3,520	−4,150	−19,220	−30,930

W. H. Steele gave 4·70 millivolts at 100° for the thermoelectric force of the *platinum-antimony* couple ; and observations were made by A. V. Tidblom. W. Jäger and H. Diesselhorst gave −6·52 millivolts at 100° for the *platinum-bismuth* couple ; J. Dewar and J. A. Fleming, −7·25 millivolts ; and E. Wagner, −7·39 millivolts. Observations were also made by A. V. Tidblom, A. von Fitzgerald-Minarelli, and J. P. Joule. A. Blondlot measured the thermoelectric force of the *platinum-selenium* couple ; and L. W. Austin, and A. Teichmann, that of the *platinum-tellurium* couple. H. Pécheux gave for the thermoelectric force of the *platinum-tantalum* couple between 0° and 400°, $dE/d\theta=0\cdot26+0\cdot0048\theta$ microvolt. The couple was discussed by A. Schulze, who also studied the *platinum-molybdenum* couple, and the *platinum-tungsten* couple.

E. Wagner gave 0·82 millivolt at 100° for the thermoelectric force of the *platinum-manganin* couple, and W. Jäger and H. Diesselhorst gave 0·57 millivolt. Observations were made by O. Knopp. W. Jäger and H. Diesselhorst gave for the thermoelectric force of the *platinum-iron* couple 1·45 millivolts at 100° ; J. Dewar and J. A. Fleming gave 1·91 ; and E. Wagner, 1·77 millivolts. H. le Chatelier gave $-16\cdot6\theta+0\cdot0096\theta^2$ between 0° and 700°, and $-2\cdot5\theta-0\cdot0105\theta^2$ between 700° and 1000°. P. G. Tait gave 519° for the neutral point. Observations were made by H. V. Regnault, J. M. Gaugain, A. Abt, G. Belloc, O. Knopp, O. Boudouard, C. Benedicks, W. Broniewsky, C. S. M. Pouillet, A. C. Becquerel, C. A. Young, and B. Franz—*vide* iron, **13**. 66, 1934. For the thermoelectric force of the *platinum-cobalt* couple, K. Noll gave −1·52 millivolts at 100°, and G. Reichard, −1·99 millivolts. Observations were made by O. Knopp. For the *platinum-nickel* couple W. Jäger and H. Diesselhorst gave −1·62 millivolts at 100° ; J. Dewar and J. A. Fleming, −1·43 ; K. Noll, −1·65 ; E. Wagner, −1·52 ; G. Reichard, −1·94 ; and K. Feussner and St. Lindeck, −1·20 millivolts. W. Rohn also studied the subject. R. von D. Wegner, and K. E. Grew measured the effect with nickel (*q.v.*), and with nickel-copper alloys. J. T. Bottomley and A. Tanakadate measured the thermoelectric force of the *platinum-platinoid* couple ; A. Abt, of the *platinum-nickel-silver* couple ; and for the *platinum-constantan* couple, G. Reichard gave −3·30 millivolts at 100° ; W. Jäger and H. Diesselhorst, −3·44 ; E. Wagner, −3·47 ; and K. Feussner and St. Lindeck, −3·04 millivolts. O. Berg gave

	−69·8°	−11·8°	0°	58·3°	80·9°	102·4°
E.m.f. .	0·002416	0·000668	0·000300	0·00151	(0·00206)	0·003145 volt

W. Goedecke studied the thermoelectric force of platinum against various platinum alloys ; and the thermoelectric force of platinum against other metals has been also discussed previously, in connection with the metals and their alloys ;

and for the thermoelectric force of platinum against the other platinum metals, *vide infra*.

A. Walcker, and L. Nobili observed that in cold water hot platinum is positive against cold platinum, also in sulphuric acid (1 : 2), in soln. of sodium chloride (1 : 10 and 1 : 100), but negative in soda lye. F. C. Henrici said that the hot metal is positive in soln. of sulphuric or nitric acid, ammonium chloride, potassium iodide, cupric chloride, mercuric nitrate, stannic chloride, and ferric chloride or sulphate; and negative in water, hydrochloric acid, potassium hydroxide, chlorate, carbonate or sulphate, sodium carbonate, copper sulphate, silver nitrate, ferrous chloride or sulphate, acetic acid, oxalic acid, very dil. soln. of sulphuric or nitric acid, barium chloride, mercuric chloride, manganous chloride, and potassium ferrocyanide. Observations were made by M. Faraday, A. Voller, H. Wild, A. C. Becquerel, G. Gore, B. Kaniewsky, and R. Kremann and co-workers. E. Bouty studied the thermoelectric force of platinum against platinic chloride. The thermoelectric force against some fused salts and glass was studied by R. Böttger, T. Andrews, and W. G. Hankel.

The Peltier effect was studied by E. Edlund,[22] and H. Jahn. A. E. Caswell gave 0·85. P. W. Bridgman measured the Peltier effect, $P\times10^6$ joules per coulomb, with platinum, uncompressed metal and metal compressed at p kgrms. per sq. cm., and found:

	P	0°	20°	40°	60°	80°	100°
$P\times10^6$	2,000	7·7	10·3	12·8	13·7	12·7	10·1
	6,000	23·0	32·2	37·0	37·6	36·6	35·1
	12,000	44·8	64·8	76·0	76·6	72·3	64·9

or $P\times10^6=(-3{\cdot}092-0{\cdot}02668\theta)(\theta+273)$ volts for one sample of platinum against lead, and for another specimen, $P\times10^6=(-1{\cdot}788-0{\cdot}0346\theta+0{\cdot}0_3126\theta^2)(\theta+273)$ volts. J. Gill also measured the Peltier effect between platinum and dil. sulphuric and nitric acids, and soln. of sodium chloride and potassium bromide and sulphate.

According to O. Berg, the **Thomson effect** is negative, and changes only a little with temp., and he found that $\sigma\times10^6=8{\cdot}79$ to $9{\cdot}69$. Lord Kelvin observed that the heat flows from the warmer to the colder parts in the direction of the current. The subject was studied by E. H. Hall, C. Benedicks, W. König, F. P. le Roux, H. Haga, and J. Weiss. According to P. W. Bridgman, $\sigma\times10^6=0{\cdot}02668(\theta+273)$ volts per degree for one sample of platinum against lead, and $\sigma\times10^6=-0{\cdot}0346-0{\cdot}0_3252\theta(\theta+273)$ volts per degree for another sample. For a platinum couple made of uncompressed metal and metal compressed at p kgrms. per sq. cm., the Thomson heat effects, $\sigma\times10^8$ joules per coulomb per degree, were:

	p	0°	20°	40°	60°	80°	100°
$\sigma\times10^8$	2,000	10·9	10·0	5·0	−6·3	−13·4	−19·8
	6,000	49·2	24·6	1·6	−13·3	−18·3	−17·9
	12,000	95·7	61·9	2·5	−36·0	−48·6	−59·0

According to E. W. Hall,[23] the **Hall effect** at 20° is 2·4 when that of iron is −78; gold, 6·8; and tin, 0·2. A. von Ettingshausen and W. Nernst gave −0·00024 for the Hall coeff.; H. Zahn, −0·000127; J. Königsberger and G. Gottstein, −0·000200; and A. W. Smith, 0·000202. P. Raethjen gave for platinum foil, −0·000230 at 20° and 10,500 gauss. W. Frey, and H. Alterthum observed that the metal at a high temp. shows a very small temp. coeff. for the Hall effect:

	225°	450°	680°	1025°	1300°	1500°
Hall effect $\times10^6$	−194	−201	−210	−234	−264	−280

but A. W. Smith observed a value −0·000202 at 20°, and 0·000222 at −190°. H. Alterthum found that the curve representing the Hall effect at different temp. has a minimum between 83° and 194°. H. B. Peacock obtained for thin films −0·000130 at 18°. Observations were made by P. Raethjen, A. Riede, A. K. Chapman, M. Cantone, and E. Bossa. H. Zahn gave -21×10^{-9} for **Leduc's effect**, and A. K. Chapman studied the **Carbino effect.**

Observations on the **magnetic properties** of impure platinum were made by J. P. Dessaignes,[24] F. Gobel, and P. Dulk. O. J. Broch and co-workers, and M. Faraday considered the purified metal to be feebly magnetic. J. Königsberger gave 29×10^{-6} vol. unit for the **magnetic susceptibility** of platinum, and W. Finke gave $22{\cdot}6 \times 10^{-6}$. K. Honda gave $1{\cdot}132 \times 10^{-6}$ mass unit at 18°, and $0{\cdot}7 \times 10^{-6}$ at 1000°; J. Königsberger, $1{\cdot}35 \times 10^{-6}$; Y. Shimizu, $1{\cdot}08 \times 10^{-6}$; and A. E. Oxley gave $64{\cdot}3 \times 10^{-7}$ mass unit for platinum-black, and $14{\cdot}7 \times 10^{-7}$ mass unit for hydrogenized platinum-black—*vide infra*. The decrease with rise of temp. is slower than corresponds with Curie's law—*vide* iron. A. Kussmann discussed the subject. Y. Shimizu studied the effect of stress on the magnetic susceptibility. A. N. Guthrie and L. T. Bourland found that up to 427°, the magnetic susceptibility of platinum follows the Curie-Weiss rule, and the deviation is referred to an underlying diamagnetism independent of temp. M. Owen, E. C. Wiersma, and H. du Bois and co-workers studied this subject. F. W. Constant, and F. E. Lowance and F. W. Constant studied the effect of cold work on the magnetic susceptibility. According to H. F. Biggs, the magnetic susceptibility is diminished by absorbed hydrogen so that the saturated metal would probably be diamagnetic. J. Lamont, and S. H. Christie made observations on the magnetic induction. S. Meyer gave $0{\cdot}227 \times 10^{-6}$ for the atomic magnetism. R. C. Loyarte, C. Sadron, P. Weiss, P. Weiss and G. Foëx, T. Schmidt, and P. Collet and G. Foëx discussed the magnetic moment of platinum; B. Cabrera and A. Dupérier, the atomic magnetism $Pt^{\cdot\cdot}$, $-17{\cdot}4 \times 10^{-6}$ c.g.s. unit; E. C. Stoner, the spin paramagnetism; and R. Becker and R. Landshoff, D. M. Bose and H. G. Bhar, J. A. Christiansen and R. W. Asmussen, E. Vogt, W. Kopp, G. Foëx, and W. Klemm and co-workers, the magnetic properties of some platinum compounds. O. Goche studied the effect of a magnetic field on cathodic evaporation. A magnetic field at right angles to the current, flowing between platinum electrodes in an aq. soln. of an electrolyte, alters the current. F. H. Loring studied the subject. J. Dorfman and R. Jaanus studied the rôle of conductivity electrons in ferromagnetism.

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§ 14. The Chemical Properties of Platinum

A. Jaquerod and F. L. Perrot,[1] F. Soddy, H. Damianovich, and H. Damianovich and J. J. Trillat, observed that platinum absorbs a small proportion of **helium.** W. Ramsay, and M. W. Travers observed that helium does not diffuse through heated platinum. H. Damianovich and co-workers, and J. Piazza studied the action of helium. A. Féry observed the effect of helium adsorption on the resistance of the metal. According to R. Salvia, cathodic spluttered platinum deposited in the presence of helium has a face-centred cubic lattice, and there is not space in the lattice for the entry of helium atoms. H. Damianovich noted the change in the microstructure of platinum in an electric discharge in helium. R. W. Lawson showed that platinum electrodes in helium absorb a little gas, and similar results were obtained with **neon.** W. Ramsay, and M. W. Travers found that **argon** does not diffuse through heated platinum. J. C. Stimson, and G. I. Finch and J. C. Stimson studied the subject. The adsorption of argon by platinum was observed by M. W. Travers to be very small. The absorption of argon by the electrodes in discharge tubes was discussed by L. Troost and L. Ouvrard, B. Brauner, S. Friedländer, J. M. Eder and E. Valenta, and H. Kayser; and of **krypton,** by J. N. Collie, E. C. C. Baly, and S. Valentiner and R. Schmidt, and likewise also with **xenon.** W. Ramsay and co-workers, and V. Kohlschütter and co-workers, observed no combination with helium, neon, argon, krypton, and xenon. J. N. Collie suggested the possibility of a combination with xenon. F. Fischer and co-workers observed no sign of a combination with argon when platinum is spluttered in liquid argon. W. T. Cooke, and W. Frankenburger and co-workers studied the subject. H. Damianovich and co-workers compared the action of helium on platinum in an electric discharge with the product in oxygen, nitrogen,

and hydrogen. H. Damianovich found that the rate of dissolution of platinum in aqua regia decreases with absorbed gases in the order He, O_2, N_2. P. M. Niccolini [2] discussed the odour of the element.

Ordinary platinum contains much occluded gas which is very difficult to remove. A. Berliner [3] estimated that the metal contains roughly 80 vols. of occluded gas. Platinum freed from occluded gases can be readily recharged with gas. L. Mond and co-workers found that platinum foil at ordinary temp. gives off very little gas, but at dull redness it gives up 0·4 times its vol. of gas—chiefly carbon dioxide. B. Delachanal observed:

	H_2	CH_4	CO	CO_2	N_2
144 grms. Pt . .	3·65	0·47	4·05	0·70	1·31—10·20 c.c.
146 grms. Pt–Ir .	3·65	0·87	3·60	0·60	1·08— 9·80 c.c.

150 grms. of platinum black occluded 17 c.c. of gas—15·3 c.c. were absorbed by potash lye, and the remainder was incombustible. D. Tommasi gave for the absorption coeff. 1·75 for **hydrogen,** 9·35 for oxygen, 9·42 for sulphur dioxide, and 65·00 for carbon monoxide. J. L. Smith found that air condenses on smooth platinum as a film which can be removed by polishing. C. Zengelis observed that when hydrogen is passed into a liquid in which platinum is immersed, the metal adsorbs hydrogen.

The absorption of hydrogen by the platinum metals was noted by H. Becquerel, K. Fischbeck, A. Frumkin and co-workers, G. F. Hüttig, W. Frankenburger and co-workers, W. G. Palmer, J. C. Stimson, T. Wilm, and F. Winteler. A. Sieverts observed that the solubility of hydrogen in compact platinum is very small. A. Mior said that platinum can take up 8·4 times its vol. of hydrogen, but it takes a very much longer time to saturate the metal at ordinary temp. than it does at a higher temp. A. Sieverts and E. Jurisch found that equilibrium is attained very rapidly at a high temp. M. Bodenstein also reported an appreciable solubility at room temp., but A. Sieverts and E. Jurisch thought that some observations must have been misinterpreted, since they found that 100 grms. of compact platinum absorbed at

	409°	827°	1033°	1136°	1239°	1342°
Hydrogen . . .	(0·006)	0·009	0·021	0·036	0·055	0·084 mgrm.

These results compared with those for nickel are represented by the curves in Fig. 17. T. Graham observed that at a red-heat platinum absorbs hydrogen and retains it tenaciously at ordinary temp., but it gives off the gas at a red-heat in vacuo. The metal does not change its appearance when it absorbs the hydrogen, but after driving off the gas, it appears to be covered with bubbles. At a red-heat 1 vol. of platinum absorbs 0·17 vol. of gas; platinum black absorbs 1·48 vols. Platinum foil which absorbed 0·76 vol. of hydrogen in 3 hrs. at 100°, absorbed 1·45 vols. at 230°. One vol. of platinum wire made from molten metal absorbs 0·128 to 0·207 vol. of hydrogen at a red-heat; worked platinum (old crucible), 3·83 to 5·53 vols.; worked platinum (old tube), 2·28 to 2·80 vols.; and platinum black, 1·48 vols. Observations were also made by M. Berthelot, A. Mior, W. Odling, W. Skey, L. Anelli, F. H. Pollard, and A. Berliner. The observations of M. C. Boswell, and M. C. Boswell and R. R. McLaughlin, were vitiated by the use of a leaky apparatus. H. Damianovich and C. Christen studied the action of hydrogen at a low press., and under the influence of an electric discharge. G. Kernot and F. de S. Niquesa studied the absorption of hydrogen by colloidal platinum—*vide supra*; and S. H. Barstow, by thin films of platinum.

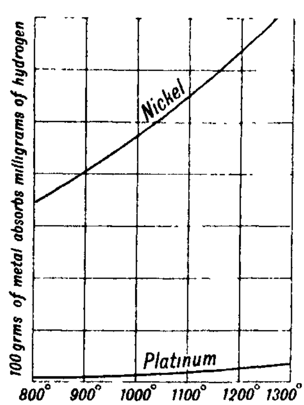

FIG. 17.—The Absorption of Hydrogen by Platinum.

M. von Pirani and A. R. Meyer found drawn platinum does not take up hydrogen at a red-heat. When platinum is heated to a high temp. in hydrogen, the m.p. is depressed 250° to 300°, and the metal becomes brittle. The effect is not due to the occlusion of hydrogen but rather to the presence of a small quantity of a carbonaceous impurity in the hydrogen from which, at or near its m.p., the metal takes carbon. A. Sieverts and W. Krumbhaar showed that molten platinum probably dissolves hydrogen.

T. Graham also found that when platinum is used as the cathode in the electrolysis of water, it can take up as much as 2·19 vols. of hydrogen which is given up at a red-heat in vacuo, or when the hydrogenized metal is used as anode in the electrolytic cell. F. Winteler observed that when spongy platinum is used as cathode, some of the absorbed gas is given off when the circuit is broken. The absorption of electrolytic hydrogen was studied by H. Schlesinger, L. Cailletet and E. Collardeau, A. E. Freeman, E. Root, J. Eggert, M. A. Schirmann, and J. R. Partington.

According to A. Sieverts and E. Jürisch, the absorption of hydrogen by compact platinum at a high temp. is probably a case of simple dissolution, but in the case of platinum black, chemical changes supervene. M. W. Travers, and W. Heald studied the absorption of hydrogen by platinum obtained by cathodic spluttering, and R. Burstein and A. Frumkin, by platinized charcoal. G. Neumann and F. Streintz observed that platinum black takes up 49·30 times its vol. of hydrogen, and G. Neumann, 63·14 to 77·14 vols. L. Mond and co-workers found that under reduced press. platinum black absorbs a certain vol. of hydrogen, and more is absorbed as the press. is raised to 200 or 300 mm., and a further increase of press. is almost without effect since by increasing the press. from 1 atm. to 4½ atm., only one more vol. of hydrogen is absorbed. About 310 vols. of hydrogen are absorbed per unit vol. of platinum black, and of this, 200 vols. are converted by the absorbed oxygen into water, so that only 110 vols. are really occluded by the platinum. Part of the hydrogen can be removed at ordinary temp. in vacuo, and by far the larger proportion at about 250° to 300°, but a red-heat is necessary for its complete removal. The amount of hydrogen absorbed by platinum is very largely influenced by slight traces of impurity. E. Müller and K. Schwabe observed that the quantity of occluded hydrogen depends on the temp. of formation of the metal from its oxide; on the method of preparing the oxide, and on the rate at which the hydrogen is brought in contact with the metal. The freshly-prepared metal can absorb more hydrogen than is the case with the metal which has been kept for some time. L. Mond and co-workers also observed that platinum sponge obtained by heating platinum black to redness has a greater absorption power than platinum sponge made by heating ammonium chloroplatinate. A. de Hemptinne also noted that platinum black which has been heated to 180° suffers a reduction of absorptive power. H. S. Taylor and R. M. Burns found that the number of vols. of hydrogen taken up by 1 vol. of

	25°	110°	218°
Platinum sponge	4·05	4·50	4·90
Platinum black	6·85	6·00	4·90

A. F. Benton said that it was here assumed that the absorbed hydrogen is all removed at 110° in vacuo; actually, more than half the absorbed hydrogen is retained by the metal under these conditions. He gave 36·7 vols. as the average absorption by 1 vol. of platinum black at 25° and 1 atm. press. H. S. Taylor and R. M. Burns noted that the absorption power depends on the mode of preparation and is less pronounced the higher the temp. of preparation. R. Burstein and A. Frumkin studied the absorption of hydrogen by platinized charcoal. E. Müller and K. Schwabe observed that the platinum can adsorb initially more hydrogen than is the case if the metal has been degassed before it is allowed to re-adsorb the gas. E. B. Maxted's results on the effect of age on the absorption are summarized in

Fig. 18. A. Sieverts and H. Brüning's curve for the speed of absorption of hydrogen by platinum black prepared by the reducing action of magnesium is shown in Fig. 19, for 25° and also for —20°. E. B. Maxted and N. Hassid observed that with 12 grms. of platinum the rates of absorption with different initial concentrations of hydrogen decrease as the absorption concentration at which the gas is added increases. A. F. Benton's curves for the rates of approach to equilibrium at different temp. and pressure, with 4·269 grms. of platinum at 737·7 mm. and at 774·3 mm., are shown in Fig. 20. T. Wilm noted the evolution of heat during the absorption of hydrogen by platinum black, and P. A. Favre observed that the heat developed in the early stages of the absorption is 23·075 cals. per eq. of hydrogen, and in the later stages, 13·528 Cals. L. Mond and co-workers could not confirm this result. The decrease in the values is connected with the union of the hydrogen with the oxygen already occluded by the metal. They gave 68·8 Cals. per gram of hydrogen, or 137·6 Cals. per mol of hydrogen. According to E. B. Maxted, the differential heat of adsorption rises from a low value to a maximum, and finally decreases with further adsorption. The results for two specimens are summarized in Fig. 19. H. S. Taylor

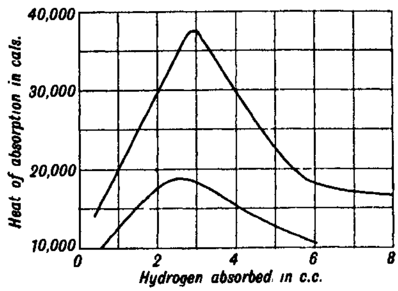

FIG. 18.—The Heat of Absorption of Hydrogen by Platinum Black.

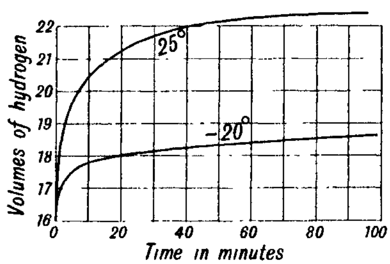

FIG. 19.—Rates of Absorption of Hydrogen.

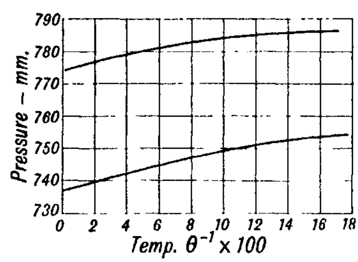

FIG. 20.—Rates of Approach to Equilibrium.

and R. M. Burns obtained curves which exhibited no maximum, but gradually decreased with an increase in the adsorption concentration; and E. B. Maxted and N. Hassid found that the differential heat of adsorption on platinum is nearly constant between 13,300 and 17,500 cals.; the heat of desorption also was nearly constant between —15,000 and —19,100 cals. G. B. Taylor and co-workers gave 20,000 cals. (approx.) for the heat of adsorption of hydrogen. The subject was studied by E. W. Flosdorf and G. B. Kistiakowsky, P. A. Favre, and A. Montier.

A. de Hemptinne found that platinum black absorbs less hydrogen at —78° than it does at 15°, and if the absorption tube at —78° be allowed to regain a higher temp., a marked absorption of gas occurs at about —40°. Freshly-prepared platinum black has a great absorptive power even at the temp. of liquid air—it can induce the union of hydrogen and oxygen at —190°. A. Gutbier observed a small maximum in the absorption curve at 0°. E. Harbeck and G. Lunge said that when platinum black saturated with hydrogen is cooled from 250°, it takes up the same amount of hydrogen as was given off in raising the temp. H. Baerwald found platinized asbestos absorbs more hydrogen at the temp. of liquid air than it does at room temp. F. H. Pollard also made some observations on the absorptive power of platinized asbestos. The gas molecules which bombard the metal are partly absorbed and partly reflected. The molecules which make non-elastic

collision will be adsorbed if the energy developed does not exceed that of the attraction force of the surface molecules. M. Knudsen, and F. Soddy and A. J. Berry measured what has been called the accommodation coeff. or the energy of exchange between hydrogen and platinum and obtained 0·24 at room temp., and 0·25 at —75°. H. H. Rowley and K. F. Bonhöffer obtained 0·22 at room temp., and 0·37 at —163°. The result with parahydrogen was 10 per cent. smaller at —133°, and at —93°, 15 per cent. smaller than for ordinary hydrogen. N. L. Koboseff and W. L. Anochin studied the subject. A. Sieverts and H. Brüning observed that 2·017 grms. of platinum black, prepared by reduction with formaldehyde, and occupying 0·094 c.c., at 752 mm., absorbed, at 20°, the vols. of hydrogen per vol. of platinum black indicated in Fig. 21. The results with platinum black,

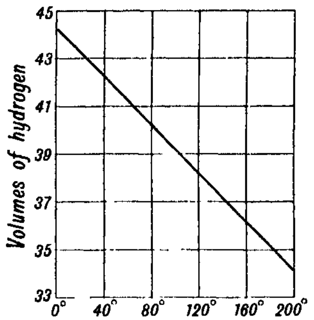

FIG. 21.—The Effect of Temperature on the Absorption of Hydrogen.

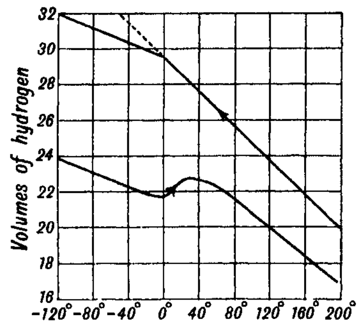

FIG. 22.—The Effect of Temperature on the Absorption of Hydrogen.

obtained by reduction with magnesium, for lower temp., are represented by the upper curve, Fig. 22, and there is a break in the curve at about 0°. The lower curve was obtained on a rising temp. with platinum black, obtained by reduction with magnesium, and degasified in vacuo at 200°, and hydrogen introduced at —120°—first under reduced press. and finally at atm. press. The temp. was then slowly raised 20° every half-hour up to 100°, and then cooled again to —120°. The absorption curve obtained is indicated in Fig. 23. The absorption isotherms were studied by W. G. Palmer.

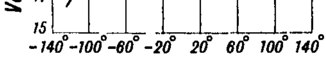

FIG. 23.—The Effect of Temperature on the Adsorption of Hydrogen.

FIG. 24.—The Effect of Ageing on the Adsorption of Hydrogen.

A. F. Benton observed that for pressures, p mm., the vol. of gas, c.c. at n.p. θ, absorbed by 4·269 of grms. of platinum black :

p	1·1	23·5	67·8	162·4	393·4	577	768 mm.
Vol. H_2 . .	6·06	6·36	6·83	6·97	7·12	7·21	7·35 c.c.

A. Sieverts and H. Brüning's results for the effect of press. on the absorption at different temp. are summarized by the curves, Fig. 25, with platinum reduced by magnesium ; the dotted curves represent the results with platinum black reduced

by formaldehyde. The adsorption curve has the form $x=ap^{1/n}$, or $x=ap^{0.12}$. W. R. Ham, and G. Borelius gave more complicated expressions.

Observations showing the diffusion of hydrogen in platinum were made by T. Graham, H. von Helmholtz, M. Bodenstein, H. Reischauer, V. Lombard, E. Waldschmidt-Leitz and F. Seitz, G. C. Schmidt and T. Lücke, W. W. Randall, V. Lombard, R. Köhler, G. Borelius, A. E. Freeman, M. Thoma, A. L. Ferguson and G. Dubpernell, F. H. Pollard, and W. Nernst and F. Lessing. R. Jouan compared the rates of diffusion of H^1 and H^2. A. Winkelmann observed that the rate of diffusion increases after the platinum has been heated some time, and that this is due not to the expulsion of occluded air, but rather to the crystalline structure assumed by the metal. The diffusion of hydrogen through red-hot platinum is not proportional to the press. of the gas; and it is probable that the diffusion is accompanied by a dissociation of the molecules so that only atoms of hydrogen diffuse in the metal. Analogous results were obtained with palladium. O. W. Richardson and co-workers found that the rate of diffusion is proportional to the square root of the press., and they also assume that it is atomic hydrogen which diffuses in the metals. W. C. Heraeus and W. Geibel studied the diffusion of hydrogen through red-hot platinum crucibles; the hydrogen present in the inner zone of the Bunsen flame diffuses through the hot platinum into the interior of a platinum crucible heated in this part of the flame. This hydrogen can reduce very energetically; thus, ferric oxide is partially reduced to iron, magnesium sulphate to sulphide, sodium sulphate to sulphite, etc. Consequently, a platinum crucible containing anything which on reduction would yield a substance capable of attacking platinum may be destroyed if heated in the inner zone of a Bunsen flame.

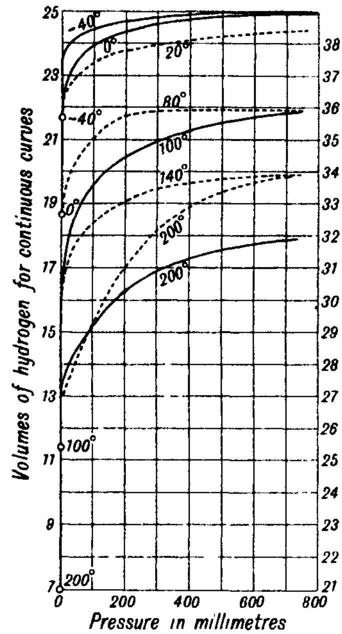

FIG. 25.—The Effect of Pressure on the Adsorption of Hydrogen.

M. Traube assumed that a **platinum hydride** is formed when platinum is used as a catalyst in hydrogenation reactions; and similarly with T. Graham, L. Troost and P. Hautefeuille, and M. Berthelot. J. H. Gladstone and A. Tribe also suggested that part of the hydrogen occluded in platinum is chemically combined, and L. Wöhler came to a similar conclusion. F. Winteler found that when a film of platinum on glass in hydrochloric acid is touched with a piece of zinc, a dark film with a metallic lustre immediately forms on the surface of the acid, and he regarded this as a platinum-hydrogen alloy. R. Engel showed that when platinum hypophosphite, suspended in water, is treated with copper sulphate, some platinum passes into soln. and some platinum hydride, as well as copper hydride, is formed. H. A. Wilson suggested that a platinum hydride, stable at a high temp., is formed when an electrical discharge is sent through hot platinum electrodes in hydrogen. F. Mohr, H. Moissan, and G. F. Hüttig studied the subject. The discontinuity in the temp. of an electrically heated wire and the absorption of heat was attributed by A. Farkas and H. H. Rowley to the formation or decomposition of hydrides.

M. Berthelot showed that spongy platinum absorbs several times its vol. of hydrogen, forming a hydride which is not decomposed at 200°, only 1 vol. of gas being expelled at that temp. When oxygen in the cold is passed into the evacuated globe containing the hydride, water is formed, with evolution of 50 Cals. per 16 grms. oxygen, from which it may be deduced that 1 grm. of hydrogen

absorbed by spongy platinum and capable of being oxidized in the cold by free oxygen, evolves 9·5 Cals. Platinum black prepared by reducing a soln. of a platinum salt with formic acid, does not evolve any gas when heated to 500° or 600° in vacuo, 62·255 grms. of the platinu mblack absorbed 0·0342 grm. hydrogen in the cold, with evolution of 14·2 cals. per grm. of hydrogen absorbed, and formation of two hydrides: in vacuo this loses 23 c.c. or 0·02 grm. hydrogen, and on passing oxygen over it, the increase of weight is 0·0765 grm. with development of 51·6 Cals. per 16 grms. oxygen, which is equivalent to 0·0091 grm. of hydrogen. Consequently, 0·0226 grm. of hydrogen, or nearly two-thirds of the gas, remains as a hydride, which is not oxidized by oxygen in the cold. This hydride is decomposed by gradually heating it to the temp. at which glass softens. The heat of formation of the less stable hydride is +8·7 Cals., H=1 grm., that of the more stable being nearly double, or +17 Cals. The proportion of the total weight of hydrogen absorbed to platinum=1 to 20, while in the more stable hydride it is 1 to 30. Platinum black prepared by reducing platinum in alkaline soln. always contains oxygen possibly as suboxide. The hydrogen absorbed is used partly in the reduction of the oxide, partly in the formation of hydride. The absorption of hydrogen in this case is attended with the evolution of +12 Cals. per grm. of gas absorbed, but a small quantity of water is formed at the same time. Of the hydrogen absorbed, one-fifth is oxidized by oxygen in the cold, whilst four-fifths require a higher temperature. H. Dobretsberger studied the effect of absorbed hydrogen on the high-frequency resistance; and G. Tammann, of cold-work. Observations on the heat of absorption were made by P. A. Favre, but E. Rothe did not think the results were accurate. H. S. Taylor, E. Waldburger, L. P. Hammett and A. E. Lorch, and O. Schmidt studied the activation of hydrogen by platinum.

E. C. Auerswald, and C. Paal and C. Auerswald prepared a colloidal soln. of platinum hydride by treating a colloidal soln. of platinum, protected by sodium lysalbate, alternately with hydrogen and exposure to air. When the **hydrosol of platinum hydride** is shaken with mercury, a hydrosol of platinum amalgam and free hydrogen are formed. N. Bach studied the properties of suspensions of platinized carbon. The state of the absorbed hydrogen was discussed by H. Schröder. L. Mond and co-workers observed no evidence in favour of the assumption that definite platinum hydrides, $Pt_{30}H_3$ or $Pt_{30}H_2$, are formed.

E. Bose concluded that the gas absorbed by the cathode is wholly or partially dissociated into single atoms. It is inferred that the catalytic activity of platinum in hydrogenation reactions is due to the accumulation of hydrogen ions at the surface of the metal, and therefore the seat of the catalytic activity is in the neighbourhood of the surface, and not in the metal itself. The subject was discussed by E. Müller and K. Schwabe, E. B. Maxted and G. J. Lewis, G. Bredig and R. Allolio, P. Anderson, G. Vavon, F. Horton and A. C. Davies, V. S. Sadikoff and A. K. Mikhailoff, R. Köppen, T. Kariyone, M. C. Boswell and C. H. Bayley, L. Kandler and C. A. Knorr, M. Calvin, and G. Vavon. Y. Venkataramaiah and M. V. N. Swamy noted that hydrogen is activated by diffusion through platinum. I. Langmuir showed that probably the surface of the platinum, at press. below 1 bar, is covered with a layer of gas of the thickness of 1 atom or 1 molecule. This layer is not removed at 360°, and there is very little more absorption when the press. is raised to 200 bars, because layers thicker than a molecule are not formed. The metal is saturated where a unimolecular layer is formed. On this assumption, A. F. Benton said that the mol. vol. of platinum black is approximately 9·30, and therefore, the vol. occupied by each platinum atom is $1·53\times10^{-23}$ c.c., and the area assignable to each atom in a platinum surface is $6·2\times10^{-16}$ sq. cm. There are then $1·6\times10^{15}$ atoms per sq. cm., and if the assumption be made that each platinum atom on the surface holds 1 *atom* of adsorbed gas, there must be $0·80\times10^{15}$ mols. of hydrogen or carbon monoxide adsorbed per sq. cm. of surface. In other words, $3·0\times10^{-5}$ c.c. of gas is required to form 1 sq. cm. of such an adsorbed layer. A. F. Benton observed an average of 37·3 c.c. of hydrogen per c.c. of

platinum, and hence inferred that the platinum black had a surface area of 1.3×10^6 sq. cm. per c.c., or 6·0 sq. metres per gram. The subject was discussed by A. Eucken, and M. Polanyi. E. Müller and K. Schwabe observed that of the hydrogen adsorbed by reduced platinum, 53 to 69 per cent. is irreversibly absorbed (indicating chemical combination) and the remainder is reversibly absorbed (indicating molecular penetration in the lattice or simple soln.). P. Anderson showed that hydrogen just removed from hydrogenized platinum is more chemically active than ordinary hydrogen in reducing copper oxide, and sulphur. S. Roginsky, and C. Y. Meng and co-workers studied the ionization of hydrogen gas in contact with platinum; J. Horiuchi and M. Polanyi, the ionization of hydrogen at a platinum electrode in alkali lye; and E. B. Maxted and C. H. Moon compared the ratio of adsorption of light and heavy hydrogen.

According to G. Bredig and R. Allolio, and W. Frankenburger and K. Mayrhofer, X-radiograms show that the space-lattice expands 0·9 per cent. when the metal has absorbed the gas. A. Osawa found that the arrangement of the atoms in the space-lattice of platinum black is not changed by the absorption of hydrogen, but there is a linear expansion of 2·4 per cent. indicating that the gas enters into the space-lattice of the metal. F. Horton and A. C. Davies found that positive ions were produced when a positively charged plate is bombarded with electrons with a minimum velocity corresponding with 13 volts, and the effect is due not to hydrogen, but to platinum. L. V. Pisarshevsky supposed that the catalytic action and in hydrogenation is due to the splitting of the hydrogen atom into electron and proton. The subject was studied by B. Batscha, J. E. Nyrop, and R. Adams and co-workers. K. and L. Packendorff studied platinum as hydrogenation and de-hydrogenation catalyst. G. I. Finch and J. C. Stimson, and N. R. Dhar inferred that ions are emitted by platinum when it absorbs a gas, and these ions account for the catalytic activity of the metal. G. Bethe studied the effect of platinum on the photoelectric properties of hydrogen; and A. Féry, the effect of hydrogen on the electrical resistance. K. Bennewitz and P. Günther found that the resistance of platinum wire at 750° to 850° decreases during the absorption of hydrogen, and increases when the gas is extracted. The change in resistance depends on the temp. and, somewhat below 1200°, the change is very slight. At higher temp., the resistance increases during the absorption of hydrogen; this is accompanied by the formation of larger metal crystals, a loosening of the texture of the metal, and a diminution in contact between the individual crystal surfaces. H. Damianovich noted the change in the microstructure of platinum after exposure to the electric discharge in hydrogen. K. F. Bonhoeffer and co-workers, and P. H. Emmett and R. W. Harkness, studied the effect of platinum on the parahydrogen conversion; P. H. Emmett and R. W. Harkness, and A. and L. Farkas, the displacement of light by heavy hydrogen; and J. Horiuchi and M. Polanyi, the distribution of heavy hydrogen between water and the hydrocarbons. C. Paal and A. Schwarz found that hydrogen is oxidized at ordinary temp. in the presence of a colloidal soln. of platinum; D. P. Smith, F. W. Reynolds, and A. Coehn and K. Sperling studied the effect on the electrical resistance; and A. Janitzky, the effect on the current passing through a vacuum tube with a glowing cathode.

S. Vassilieff and A. Frumkin observed that mercuric chloride is strongly adsorbed by platinized charcoal and is not displaced when the latter is saturated with hydrogen. The addition of a mol. of mercuric chloride per atom of platinum suffices to abolish the capacity of the charcoal to assume a higher oxygen potential, *i.e.* it adsorbs the same quantity of acid as unplatinized charcoal. In an acid medium, desorption of acid by hydrogen is not affected by the presence of mercuric chloride. If, however, the mercuric chloride is adsorbed from an alkaline solution, or is previously "fixed" by means of hydrogen, the platinum is poisoned and desorption of acid is incomplete. Reduction of adsorbed oxygen by means of hydrogen is also inhibited under similar conditions. Mercuric chloride influences only slightly the development of a hydrogen potential by oxygen-free charcoal.

F. P. Bowden and E. K. Rideal, F. W. Reynolds, and O. Erbacher studied the active surface of platinum; G. Käb, the influence of adsorbed gas on the catalytic activity; and J. C. Stimson, the electrical state of the metal.

O. Loew and K. Aso [4] observed that when moist platinum black has been exposed to air for some time, it contains nitric acid and traces of ammonia. J. W. Döbereiner, and T. J. Pelouze and E. Frémy showed that compact platinum absorbs **oxygen** when heated to a high temp. Neither T. Graham, nor T. Wilm detected any absorption of oxygen when platinum is heated in air. A. Sieverts found a little oxygen is taken up by a platinum wire heated in oxygen; G. Bodländer and K. Köppen said that oxygen is absorbed between 700° and 900°; C. Langer and V. Meyer noted an absorption occurs at 1690°; and E. Goldstein, at a white-heat. The absorption of oxygen was also observed by A. Magnus, E. F. Smith, V. A. Roiter and M. G. Leperson, J. C. Stimson, G. I. Finch and J. C. Stimson, B. Neumann and E. Goebel, L. H. Reyerson and L. E. Swearingen, H. Reischauer, and L. Holborn and F. J. Austin; and E. Bose said that the absorption is due to a process of solution, and not to the formation of a compound. R. Lucas said that purified platinum does not absorb oxygen, but platinum containing iridium does not do so with activated oxygen. R. Schwarz and W. Kunzer found that an oxide is formed. F. E. Carter said that the finely-divided metal, in oxygen, begins to form black platinum monoxide at 450°, that this oxide at 500° forms platinum and its dioxide, and that the dioxide at 500° furnishes platinum and oxygen. According to E. K. Rideal and O. H. W. Jones, the loss in weight of a platinum wire heated electrically, to 1400° K. to 1900° K., in a glass bulb immersed in liquid air, is greater in oxygen than in vacuo. This is in agreement with the observations of R. Nahrwold, G. Owen, W. Stewart, and J. Elster and H. Geitel. E. K. Rideal and O. H. W. Jones infer that two reactions are involved: (i) a surface reaction between the platinum and oxygen at a rate which is directly proportional to the press., p, of the oxygen; and (ii) a reaction which occurs simultaneously between the platinum vapour and the oxygen. The combined effect is represented by the equation $-dp/dt=a+bp$, where a and b are constants. Below 1700° K., and above that temp. when p is less than 50 bars, the second reaction: $Pt+O_2=PtO_2$, predominates. I. Langmuir suggested that the alteration in the speed of the reaction at high press. and temp. is due to the concentration of ozone, or of oxygen atoms, but E. K. Rideal and O. H. W. Jones consider this to be less likely than the hypothesis of a surface reaction. H. H. Rowley and K. F. Bonhöffer found the accommodation coeff. of oxygen to be 50 per cent. higher than for hydrogen (*q.v.*). H. Damianovich and J. Piazza studied the action of hydrogen at a low press. under the influence of an electric discharge. H. Damianovich observed that platinum with adsorbed gases dissolves at a lower speed in aqua regia. R. Schwarz and W. Kunzer found that with activated hydrogen some hydride is formed.

L. Mond and co-workers found that although platinum foil at ordinary temp., or at a red-heat, does not absorb appreciable quantities of oxygen, yet two samples of platinum sponge at a red-heat absorbed respectively 2·4, and 0·5 vol. of oxygen. Platinum black was found to absorb relatively large proportions of oxygen—about 100 times its vol. The evolution of the absorbed oxygen is appreciable at 100°, and between 300° and 400°, the rate of evolution is very great, but a red-heat is necessary for its complete removal. Curves for four different specimens of platinum black are indicated in Fig. 27. While hydrogen is given off when the metal is heated, oxygen is absorbed at temp. below 300°, and given off at 360°. A. de Hemptinne observed that platinum black always contains a considerable proportion of absorbed oxygen. G. Neumann found that at 450°, platinum takes up 63 to 77 vols. of oxygen; L. Wöhler, that when platinum black is heated six weeks at 109° to 280° in air, it takes up 2·3 per cent. of oxygen; H. S. Taylor and R. M. Burns found that 1 vol. of platinum sponge absorbed 1·90, 2·80, and 4·30 vols. of oxygen, respectively, at 25°, 110°, and 218°; and platinum black, 26·50 and 26·10 vols.

of oxygen, respectively, at 25° and 110°. A. F. Benton obtained as an average at 25° and 1 atm. press., an absorption of 20·4 vols. The rates of approach to equilibrium at different temp., θ, and press., of two samples are indicated in Fig. 26. P. Grandadam, and P. Laffitte and P. Grandadam studied the absorption of oxygen by platinum sponge or platinum black when heated in oxygen under press. A. Sieverts observed that 30·45 grms. of platinum wire heated in vacuo gave

	20°	200°	400°	600°	800°	1000°
O_2	0·11	0·11	0·14	0·18	0·18	0·29 c.c.
Time	0	35	65	80	96	110 minutes.

C. Paal and C. Amberger observed that colloidal platinum readily takes up oxygen from the air, and the elementary hydrosol is not regenerated when the sol is treated with hydrogen.

W. W. Randall found that oxygen does not diffuse through heated platinum; but A. L. Ferguson and G. Dubpernell discussed the transfer of electrolytic oxygen through the metal. J. Thomsen observed that the affinity of platinum for oxygen is small. According to I. Langmuir, a platinum filament at temperatures above 1600° K. gradually causes the removal of oxygen at low pressures. The oxygen combines with the platinum atoms as fast as they evaporate from the filament, and forms the dioxide, which collects on the bulb as a brown deposit. G. B. Taylor and co-workers gave approximately 65,000 cals. for the heat of adsorption; and E. B. Maxted and N. J. Hassid, 60,000 cals. per gram mol. of oxygen. H. St. C. Deville and H. Debray said that platinum is never found as a mineral associated with oxygen; T. Wilm noted that platinum obtained by the ignition of the ammines or ammonium salts at a red-heat in air is not oxidized; and no sign of oxidation occurs when platinum sponge is heated to redness in air. H. le Chatelier added that under suitable conditions of temp. or press., the metal may be oxidized. Y. Okayama studied the subject. W. Skey noted that the surface of the metal exposed to air liberates iodine from a dil. soln. of potassium iodide in dil. sulphuric acid; J. L. Smith also noted the condensation of air on the surfaces of platinum crucibles. According to W. Skey, platinum which has been "in contact for a short time with distilled water, ammoniated water, or with aq. soln. of the alkalies, carbonates or chlorides," will not amalgamate. Acids, on heating to about 200°, restore the amalgamable condition; and G. Meissner, H. Rumpelt, and B. Dessau showed that a film can be detected optically on platinum heated in air or oxygen—*vide supra*, the volatilization of platinum. H. Damianovich noted a change in the microstructure of platinum after exposure to the electric discharge in oxygen. A. Féry studied the effect of adsorbed oxygen on the electrical resistance.

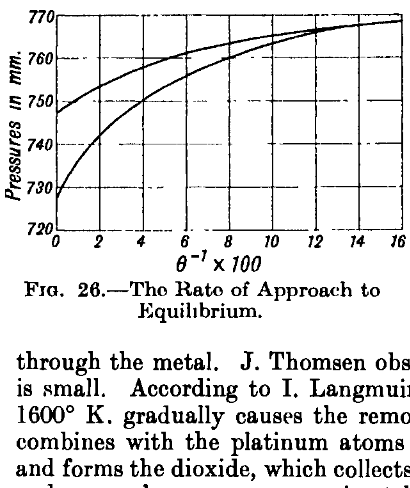

FIG. 26.—The Rate of Approach to Equilibrium.

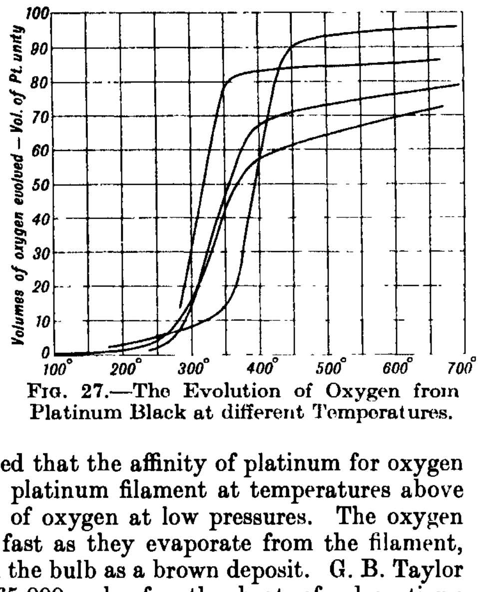

FIG. 27.—The Evolution of Oxygen from Platinum Black at different Temperatures.

The heat developed during the occlusion of oxygen by platinum was found by L. Mond and co-workers to be 11·0 cals. per gram of oxygen, and since this is almost the same as the value given by J. Thomsen for the heat of formation of platinous hydroxide, the two phenomena may be related, the necessary water being present in platinum black dried in vacuo. They finally concluded that the occlusion of oxygen by platinum or palladium is a true oxidation phenomenon. According to L. Wöhler, and C. Engler and L. Wöhler, platinum black containing occluded oxygen turns potassium iodide starch solution blue; it is somewhat soluble in dilute hydrochloric acid, the weight of platinum in solution is less than the weight of platinum black dissolved, and if the difference be attributed to oxygen it is found that the ratio of platinum to oxygen agrees well with PtO; the amount of oxide present in the platinum sponge depends on the state of division. It does not easily amalgamate, and the amalgam formed becomes covered with a film of the black oxide; hydrogen dioxide does not reduce it in the cold, but on boiling, complete reduction takes place, and it is also reduced by alcohol, ether, and other organic substances; in absence of air, it oxidizes arsenious to arsenic acid, and the residue loses its spongy character and becomes granular. It is further shown that the properties of active platinum sponge closely resemble those of platinous oxide, in confirmation of the theory of A. de la Rive that in the catalysis by platinum black, the intermediate active agent is this oxide. However, platinum sponge free from oxide causes more active oxidation than does platinous oxide, and this is explained by C. Engler and W. Wild's theory of the intermediate formation of peroxide and secondary formation of oxide, which takes place more readily with the finely-divided sponge than with the more compact platinous oxide. R. Vondracek also inferred that platinum black contains a very labile compound of platinum and oxygen; and E. Goldstein, that in the electrical discharge in oxygen with platinum electrodes, a compound of platinum and oxygen is formed, that the absorption of oxygen is very rapid if the electrodes are at a high temp., and that the faculty of platinum to form these oxides is connected with its catalytic activities. P. Laffitte and P. Grandadam found that platinum is oxidized when heated between 300° and 500° at 50 to 200 kilogrms. per sq. cm. press. At the optimum temp., 455°, spongy platinum at 4 atm. press. increased in weight 2·1 per cent.; and at 150 atm. press., 7·37 per cent., and platinum black increased 13·96 per cent. The product is a mixture of platinum monoxide and dioxide. F. C. Phillips also noted that the order of the oxidizability of the platinum metals is connected with their faculty of burning hydrogen—namely, osmium, palladium, platinum, and iridium.

Platinum black containing occluded oxygen was found by J. W. Döbereiner [5] to exert an action on hydrogen and other combustible gases or vapours whereby the metal may be heated to redness, and if air has access, the gases may be set on fire. If air or oxygen has not access, the oxidation ceases as soon as the occluded oxygen is consumed, but if air or oxygen has access, the platinum black takes up more oxygen, and transfers it to the combustible body so that the process is continuous. The subject was discussed by A. Adie, W. Artus, A. Baudrimont, A. C. Becquerel, M. Berthelot, M. Bodenstein, R. Böttger, M. C. Boswell and C. H. Bayley, C. Brunner, G. L. Cabot, H. Courcot and J. Meunier, W. Davies, J. W. Döbereiner, F. P. Dulk, P. L. Dulong and L. T. Thénard, A. Fyfe, L. W. Gilbert, F. Gill, C. A. Grüel, G. F. Hänle, H. Karmarsch, W. Klinkerfues, W. Knop, J. von Liebig, G. Merryweather, G. Merz, C. F. Mohr, F. Parmentier, C. H. Pfaff, M. V. Poljakoff and co-workers, P. W. Schmidt, C. F. Schönbein, J. S. C. Schweigger, H. A. von Vogel, A. Wagner, E. O. Wiig, and T. Wilm. A. Osawa found that the arrangement of the atoms in the lattice of platinum black is not changed by the adsorption of oxygen, but there is a linear expansion of 2·9 per cent. The inflammation of hydrogen was described by A. Garden, C. G. Gmelin, W. Herapath, and A. Pleischl; of alcohol, or ether vapour, by S. F. Dana, K. Fuchs, H. B. Miller, and G. Schübler; and the self-ignition of coal

gas, by J. Bischof,[6] W. Boehm, R. Böttger, E. Breslauer, H. Bunte, J. F. Duke, W. F. Gintl, C. Killing, J. Klaudy and O. Efrem, W. Klinger, W. Klinkerfues, J. Lewis, V. Nicolardot, E. Nowack, W. von Olderhausen, E. Orloff, F. Parmentier, J. Perl, H. Schröter, G. Sulbach, and numerous others.

K. A. Hofmann and O. Schneider [7] found the catalytic activity of the platinum metals in oxidizing hydrogen in the presence of sodium chlorate decreased in the order Pt, Rh, Ru, Pd, Au, Os, Ir, Ag. The catalysis of the reaction between hydrogen and oxygen by platinum, platinum black, platinum sponge, and colloidal platinum was discussed by M. Bodenstein, J. Böeseken and co-workers, W. A. Bone and R. V. Wheeler, M. C. Boswell and C. H. Bayley, G. Bredig and R. Allolio, D. L. Chapman and P. W. Reynolds, P. D. Dankoff and A. A. Kochetkoff, N. R. Dhar, R. P. Donnelly and C. N. Hinshelwood, E. Drechsel, C. Ernst, J. Field, G. I. Finch and co-workers, B. Foresti, W. French, A. Frumkin and co-workers, J. Gerum, W. Hartmann, A. de Hemptinne, H. Hess, K. A. Hofmann, K. A. Hofmann and co-workers, F. Hoppe-Seyler, J. Horiuti and M. Polanyi, N. I. Koboseff and V. L. Anochin, I. Langmuir, L. L. Lockrow, G. Maneuvrier and P. Chappuis, E. von Meyer, L. Mond and co-workers, W. Müller, E. Orloff, C. Paal and J. Gerum, C. Paal and A. Schwarz, L. V. Pisarschevsky, M. V. Polyakoff and P. Stadnik, H. Remy and co-workers, S. J. Roginsky and A. B. Schechter, R. Ruer, F. F. Rupert, O. Sackur, H. G. Tanner and G. B. Taylor, G. B. Taylor and co-workers, L. Vallery, R. Vondracek, E. O. Wiig, and R. Willstätter and co-workers. W. Davies discussed the rate of rise of temp. of the platinum—combustion begins at 200° ; the effect of temperature was studied by A. Berliner, A. de Hemptinne, and A. Schrotter ; the effect of pressure, by P. J. Kirkby ; the effect of X-rays, by P. H. Emmett and E. J. Jones ; the effect of light, by W. French, and P. H. Emmett and E. J. Jones ; the null-effect of X-rays, by P. H. Emmett and E. J. Jones ; the effect of retarding agents or " poisons," by S. Vasileff and F. Frumkin, N. R. Dhar, C. Moureu and C. Dufraisse, F. Krüger and E. Taege, E. W. R. Steacie and J. W. McCubbin, E. Adaduroff and co-workers, G. Vavon and A. Husson, E. B. Maxted and V. Stone, R. W. Raudnitz, R. Böttger, M. C. Boswell and C. H. Bayley, and G. Bredig and co-workers, C. Ernst, R. Höber, and W. Ostwald ; the retardation produced by overheating the carrier of the platinum catalyst, by I. E. Adaduroff and co-workers ; and the decay of activity of the colloid with time, by H. Damianovich and O. F. F. Nicola.

The oxide theory of catalysis assumes that the platinum forms an unstable oxide which is alternately reduced and re-oxidized $n\mathrm{Pt}+\mathrm{O}_2=\mathrm{Pt}_n\mathrm{O}_2$; $\mathrm{Pt}_n\mathrm{O}_2+2\mathrm{H}_2=2\mathrm{H}_2\mathrm{O}+n\mathrm{Pt}$; or $\mathrm{Pt}_n\mathrm{O}_2+\mathrm{H}_2=\mathrm{Pt}_n+\mathrm{H}_2\mathrm{O}_2$, and $\mathrm{Pt}_n\mathrm{O}_2+2\mathrm{H}_2\mathrm{O}_2=n\mathrm{Pt}+2\mathrm{H}_2+3\mathrm{O}_2$, M. Traube [8] supposed that $n\mathrm{Pt}+m\mathrm{H}_2\mathrm{O}_2=\mathrm{Pt}_n\mathrm{O}_m+m\mathrm{H}_2\mathrm{O}$, is followed by $\mathrm{Pt}_n\mathrm{O}_m+m\mathrm{H}_2\mathrm{O}_2=n\mathrm{Pt}+m\mathrm{H}_2\mathrm{O}+m\mathrm{O}_2$, and E. Oliveri-Mandala said that M. Traube's hypothesis does not explain the catalysis of ammonium nitrite, hydrazine, hydrazoic acid, and hydroxylamine ; and he assumed that the catalyst reacts with water, forming an oxide, and hydrogen. The subject was discussed by F. D. Aguirreche, T. Bayley, B. Batscha, G. Bodländer, J. Böeseken and co-workers, E. Bose, M. C. Boswell and R. R. McLaughlin, G. Bredig and co-workers, J. W. Döbereiner, J. Elster and H. Geitel, T. J. Fairley, W. French, K. Fuchs, F. Haber, R. W. Hall, K. A. Hofmann and co-workers, Kalle and Co., F. Kuhlmann, J. von Liebig, L. Mond and co-workers, E. Mulder, M. Musler, A. A. Noyes and G. V. Sammet, C. Paal and J. Gerum, T. L. Phipson, C. F. Schönbein, E. Schöne, H. H. Storch, M. Traube, A. Trillat, A. Valentini, R. Vondracek, and R. Willstätter and co-workers. The occlusion theory involving a condensation of the gas in the metal, or an activation of the hydrogen by the dissociation of the molecules into atoms, was discussed by W. M. Bayliss, G. Bredig, M. Bodenstein, H. G. Denham, H. von Euler, M. Faraday, W. French, H. von Helmholtz, V. Henri, H. Heymann, C. G. Hüfner, O. Loew, E. von Meyer, B. Neumann, and J. J. Thomson. M. Berthelot discussed the possibility of the formation of intermediate

hydrides; G. T. Beilby, P. J. Kirkby, and B. L. Vanzetti, the emission of ions by the platinum; and D. Tommasi, and O. Loew, to the evolution of thermal energy by the occlusion of the gas. The hydrogenation of organic compounds with platinum as catalyst was studied by H. S. Davis and co-workers. The poisoning of the catalyst by various gases was discussed by G. Bredig and co-workers, C. Engler and L. Wöhler, R. Höber, K. Jablczynsky, A. S. Loevenhart, O. Loew, E. Opl, R. W. Raudnitz, A. Schwarz, and L. Wöhler; and the analogy with ferments, by P. Bergell, T. Bokorny, G. Bredig and co-workers, H. Mouton, and C. F. Schönbein. V. Haas adapted H. E. Armstrong's electrochemical theory to explain the catalytic action of the platinum metals in gaseous or other systems. The catalytic power is attributed to the catalyst playing the rôle of a galvanic element.

Neither moist nor dry **ozone** acts on platinum, but A. Volta [9] showed that if the metal is charged with hydrogen, water is rapidly formed. The formation of ozone at the positive end of an electrically heated, red-hot platinum wire was discussed by V. S. M. van der Willigen, J. Elster and H. Geitel, E. St. Edme, and F. P. le Roux. C. H. L. von Babo thought that platinized asbestos in an ozone tube favoured the ozonization; A. W. Williamson, C. F. Schönbein, and E. Mulder and H. G. L. van der Meulen studied the catalytic decomposition of ozone by platinum black. H. G. Thode and A. C. Grubb studied the effect of platinum on the formation of ozone in the corona discharge. Soln. of ozone were found by R. Luther, R. Luther and J. K. H. Inglis, L. Gräfenberg, R. Kremann, M. Targetti, and A. Brand, to be decomposed catalytically by platinized platinum.

According to T. Ihmori,[10] platinum condenses **water** very slightly; the condensation disappears entirely after rubbing with leather. Old platinum may require heating to redness, probably in order to destroy a film of grease. Observations on the adsorption of water vapour were made by J. W. Smith, S. Lenher, and I. R. McHaffie and S. Lenher. A. Pockels discussed the wetting of platinum by water. L. Mond and co-workers found that platinum black dried at 100° contains 0·5 per cent. of water, and this can only be removed in a vacuum at about 400°, at which temp. the platinum black is converted, at least partially, into spongy platinum. At any given temp. the water retained by platinum black seems to be constant. *Vide supra* for the synthesis of water from its elements in the presence of a platinum catalyst. F. Foreman said that heated platinum does not decompose water. Water does not oxidize platinum, but W. Skey observed that platinum passes into a state in which it will not amalgamate with mercury when it has been in contact with water for a short time, and he attributed this fact to the formation of a film of oxide or suboxide of the metal. The decomposition of steam by red-hot platinum was studied by H. V. Regnault, and W. R. Grove. M. Traube-Mengarini and A. Scala found that a very small quantity of colloidal platinum is formed when platinum is boiled for a long time with water. L. Wöhler studied the oxidation of platinum black by the decomposition of water. W. Swientoslawsky and S. Bakowsky studied the rate of evaporation of water from a platinum surface. W. Traube and W. Lange observed the catalytic effect of the platinum metals in the decomposition of water by chromous salts. S. Lenher studied the adsorption of water vapour by platinum; and J. W. Smith, by amalgamated platinum. G. B. Taylor and co-workers gave 60,000 cals. for the heat of adsorption of water by platinum.

T. J. Fairley [11] observed that platinum readily dissolves in most acids if they contain **hydrogen dioxide.** C. Marie did not detect any action on platinum exposed to acidic or alkaline soln. of hydrogen dioxide; but with platinum black, L. Wöhler, and R. Vondracek assumed that an oxide is formed—*vide supra*. L. J. Thénard, W. Skey, and C. F. Schönbein observed that hydrogen dioxide is decomposed by contact with platinum. A. Rius studied the close relation between the potential of a platinum surface and its catalytic activity in the decomposition of hydrogen

dioxide. R. Wright and R. C. Smith compared the activity of platinum black in relation to the temp. of its preparation; R. Schwarz and M. Klingenfuss, the paralyzing effect of X-rays on the catalytic activity of colloidal platinum; and A. de Gregorio y Rocasolano, that the activity of the sol increases with age to a maximum and then decreases. W. Spring noted that polished platinum decomposes hydrogen dioxide, and R. C. Smith found that washing the surface with alcohol and water, or the presence of a film of grease, inhibits the decomposition. The change in the surface from amorphous to crystalline also decreases the catalytic activity, as in the case observed by G. Vavon. The catalytic effect with compact platinum was studied by A. von Bäyer and V. Villiger, K. Bornemann, H. Damianovich and O. F. F. Nicola, T. S. Glikman, A. de Gregorio y Rocasolano, F. Haber and S. Grindberg, V. Henri, H. Heymann, A. Kailan, G. R. Levi, E. B. Maxted and co-workers, A. R. Miro and N. G. Morales, E. Oliveri-Mandala, M. V. Polyakoff and co-workers, F. Richarz, A. Rius, V. A. Roiter and M. G. Leperson, R. Schwarz and W. Friedrich, I. I. Shukoff and co-workers, A. Sieverts and H. Brüning, J. Sirkin and V. G. Vassiléeff, R. C. Smith, S. Tanatar, J. Teletoff, M. Traube, I. I. Tschukoff and co-workers, F. Weigert, R. Wolff, and R. Wright and R. C. Smith; with platinum black, and spongy platinum, by H. von Euler, M. A. Heath and J. H. Walton, A. Sieverts and J. F. Müller, J. Weiss, and L. Wöhler; with colloidal platinum, by G. Bredig and co-workers, Y. K. Suirkin and I. N. Godneff, A. Lebedew, N. E. Ditman, L. Liebermann and W. von Genersich, and E. B. Spear—C. Paal and C. Amberger placed the colloids in the decreasing order of activity: Os, Pd, Pt, and Ir; the poisoning of the catalytic activity was studied by G. Bredig and co-workers, F. Böck, D. Gernez, A. S. Loevenhart and J. H. Kastle, C. H. Neilson and O. H. Brown, H. V. Tartar and N. K. Schaffer, G. Bredig and W. Reinders, C. Engler and L. Wöhler, J. H. Kastle and C. R. Smith, A. S. Loevenhart and J. H. Kastle, T. S. Price and co-workers, C. F. Schönbein, and L. Wöhler. The favourite theory of the catalytic activity turns on the formation of an unstable, intermediate oxide of platinum, and the subject was discussed by T. Bayley, G. Bredig and co-workers, F. Böck, C. H. Neilson and O. H. Brown, C. Engler and L. Wöhler, and L. Liebermann; there is also the occluded hydrogen theory by W. Nernst, H. J. S. Sand, G. Senter, and J. Teletoff; and the occluded oxygen theory, by H. von Euler. E. Leidié and L. Quennessen, L. Quennessen, F. C. Carter, and P. Nicolardot and C. Chatelot found that **sodium dioxide** forms an insoluble product when fused with platinum.

H. Moissan[12] observed that **fluorine** attacks platinum at 500° to 600°, forming platinum difluoride, and he observed that at ordinary temp. platinum is not attacked by purified fluorine, but it is corroded if the fluorine contains the vapour of hydrogen fluoride, or is dissolved in hydrofluoric acid. G. Gore observed that when silver fluoride is decomposed by chlorine in a platinum vessel at a red-heat, some platinic fluoride is formed; bromine under similar conditions also forms platinic fluoride; and similarly also with iodine. W. R. Hodgkinson and F. K. S. Lowndes found that **hydrogen fluoride** attacks a red-hot platinum wire. W. von Bolton found that in contact with platinum hydrofluoric acid acts rapidly on columbium, when without the platinum, heat is required. According to F. C. Carter, the attack by hydrofluoric acid in the cold is negligible.

According to A. Kemp, dry liquid **chlorine** does not attack platinum; and H. Goldschmidt observed that neither chlorine, nor charcoal saturated with chlorine acts on platinum at 250°. P. Schützenberger said that the metal is attacked at 350°. When platinum is heated in chlorine gas, the metal is attacked and platinum chloride is volatilized. The reaction was observed by F. Seelheim, V. Meyer, L. Troost and P. Hautefeuille, and W. R. Hodgkinson and F. K. S. Lowndes. According to C. Langer and V. Meyer, the action of dry chlorine on platinum increases with temp., and between 300° and a yellow heat decreases to almost zero; the action then increases as the temp. rises to 1300°, and is very energetic at 1600° to 1700°. P. Schützenberger observed that dry chlorine at 250°

acts on spongy platinum to form platinous chloride, and the reaction was studied by L. Pigeon. C. Nogareda found that chlorine forms a unimolecular adsorption layer, and that the attack by chlorine molecules between 600° and 850° furnishes $PtCl_4$; above 1200°, the attack is by chlorine atoms. G. Gore observed that when silver chloride is melted in a platinum crucible in an atmosphere of chlorine, the metal is attacked; and H. Erdmann and O. Hauser found that platinum is attacked when heated with chlorides of the alkalies or alkaline earths in a bunsen flame. For G. Gore's observations on the action of chlorine and silver fluoride, *vide supra*. C. F. Schönbein also observed that aq. soln. of chlorine attack the metal liberating oxygen; and that platinum black decomposes chlorine water catalytically with the evolution of oxygen. S. Cooke noted that platinum charged with hydrogen acts on chlorine to form hydrogen chloride; O. Ruff and H. Krug observed no action with the metal in contact with **chlorine trifluoride.**

W. R. Hodgkinson and F. K. S. Lowndes observed that a red-hot platinum wire in **hydrogen chloride** is attacked; and W. L. Dudley showed that hydrogen chloride in the presence of air or oxygen readily attacks platinum. P. Perotti, and H. Schiff noted that platinum favours the union of hydrogen and chlorine electrolytic gas; and the thermal decomposition of hydrogen chloride in the presence of platinum was discussed by W. Weldon; M. Berthelot observed no action at 550°; and M. G. Levi and O. Garavini observed that the decomposition occurs at 800° to 1100° in the presence of platinum, and at 1500°, without platinum. According to F. C. Carter, platinum is not attacked by hot or cold conc. hydrochloric acid, but T. Wilm, W. L. Dudley, and H. St. C. Deville and J. S. Stas found that precipitated platinum is soluble in hot, conc. **hydrochloric acid** in the presence of air; and C. Engler and L. Wöhler found that dil. hydrochloric acid partially dissolves platinum black in the absence of air, but if the metal is freed from occluded oxygen, it no longer dissolves. L. Wöhler found that finely-divided platinum, in an atmosphere of carbon dioxide freed from air, is slightly soluble in conc. hydrochloric acid when heated in a sealed tube at 200°. M. Berthelot found that fuming hydrochloric acid does not attack platinum in darkness, but the metal is attacked if exposed to light, and in the presence of manganese dioxide, twice as much platinum is dissolved as in its absence. H. Kinder observed that when iron is deposited electrolytically on platinum, and treated with hydrochloric acid, some platinum passes into soln. with the iron. J. W. Mallet, and C. Matignon found that the metal is slowly attacked by hydrochloric acid in the presence of air, forming, according to A. M. Vasileff, hydrochloroplatinic acid; E. Salkowsky found that the attack is favoured by hydrogen dioxide. According to P. Rudnick and R. D. Cooke, unignited platinum black dissolves in conc. hydrochloric acid in the presence of hydrogen dioxide yielding hydrochloroplatinic acid free from nitrogen compounds. H. E. Patten could detect no appreciable action of a soln. of hydrogen chloride in chloroform, carbon tetrachloride, ethyl chloride, benzene, silicon tetrachloride, stannic chloride, phosphorus trichloride, antimony pentachloride, sulphur monochloride, and thionyl chloride, and with the soln. in arsenic trichloride no greater action was observed than with arsenic trichloride alone. According to C. A. Peters, when a soln. of **sodium chloride** rests on mercury with a platinum wire connecting both liquids, mercurous chloride and sodium hydroxide are produced. C. Marie observed that an acidic soln. of **potassium chlorate** slowly attacks platinum. C. F. Schönbein found that in the presence of platinum black, **hypochlorous acid** decomposes with the evolution of oxygen, and F. Förster and E. Müller represented the reaction: $HClO=HCl+O$, accompanied by $3HClO=HClO_3+2HCl$, and by $HClO+HCl=H_2O+Cl_2$. E. Schaer noted that the oxidation of some organic substances by this acid is favoured by the presence of colloidal platinum. S. Cooke observed that hydrogenized platinum reduces soln. of **potassium hypochlorite** to the chloride. W. C. Bray found that platinized platinum favours the decomposition of **chlorine dioxide**: $6ClO_2+3H_2O=5HClO_3+HCl$. C. F. Schönbein observed that a soln. of indigo-blue is decolorized by

aq. soln. of **chloric acid** in the presence of platinum black, and similarly with an aq. soln. of **perchloric acid.** E. V. Zappi recommended a mixture of chloric acid and conc. hydrochloric acid as a solvent for platinum—the activity of the mixture is due to the liberation of chlorine: $HClO_3+5HCl=3Cl_2+3H_2O$. According to S. Cooke, hydrogenized platinum favours the decomposition of soln. of **potassium chlorate,** whilst **potassium perchlorate** is not affected. E. Schaer noted that the oxidation of some organic substances by chloric and the chlorates is favoured by the presence of colloidal platinum. C. Marie noted the attack of platinum by a soln. of potassium chlorate in N-H_2SO_4; and R. Vondracek observed that when ethyl alcohol is boiled with an aq. soln. of potassium chlorate in presence of platinum black, the chlorate is reduced, but there is no reduction in the absence of platinum. A similar reduction of chlorate takes place when dextrose is oxidized by potassium chlorate in presence of platinum black. C. F. Schönbein found that soln. of indigo-blue are decolorized by aq. soln. of potassium chlorate, in the presence of platinum black; and O. Loew and K. Aso, that soln. of potassium chlorate and perchlorate are reduced to chloride by glucose in the presence of platinum black. H. Sirk, and F. Förster and E. Müller noted that the presence of platinum favours the evolution of chlorine from a mixture of potassium chlorate and hydrochloric acid; and E. Wiederholt found that platinum black favoured the evolution of oxygen from potassium chlorate at 260° to 270°, and the action was studied by W. R. Hodgkinson and F. K. S. Lowndes, E. Baudrimont, and R. Böttger.

According to A. J. Balard, **bromine** in the cold does not act on platinum, and J. von Liebig observed no action at a red-heat. W. R. Hodgkinson and F. K. S. Lowndes observed that the attack on heated platinum is shorter than is the case with chlorine, and C. Langer and V. Meyer obtained similar results with bromine as those observed with chlorine. C. Nogareda found that above 1200°, bromine atoms attack platinum yielding platinous and platinic bromides. J. Urmston and R. M. Badger studied the photochemical reaction between bromine and platinum. R. Wagner said that soln. of bromine in water or hydrochloric acid have no action on platinum. For G. Gore's observations with silver fluoride and bromine, *vide supra.* J. Urmston and R. E. Badger studied the photochemical reaction between bromine and platinum. W. R. Hodgkinson and F. K. S. Lowndes observed that **hydrogen bromide** attacks a red-hot platinum wire. C. F. Schönbein found that a soln. of indigo-blue is decolorized by **bromic acid** in the presence of platinum black. E. Schaer noted that the oxidation of some organic substances by bromic acid and the bromates is favoured by the presence of colloidal platinum. J. S. Stas observed that molten **potassium bromide** does not attack platinum unless **potassium bromate** is also present—for G. Méker's observations, *vide infra.*

According to J. L. Lassaigne, the action of **iodine** on platinum is questionable, but with spongy platinum the heated metal forms a little iodide; and W. R. Hodgkinson and F. K. S. Lowndes likewise observed that under analogous conditions, traces of platinous iodide are formed. G. van Praagh and E. K. Rideal observed that at relatively low temp. iodine vapour does not attack the metal, but at about 1027°, the molecule of iodine dissociates, and at about 1127° the atomic iodine attacks the metal to form PtI and PtI_2. The combined rate of the reaction at lower temp. is represented by $-dp/dt=a+bp$, where p is the press. and a and b are constant. The a term is due to the formation of a unimolecular layer of PtI on the surface of the platinum, which evaporates at a rate independent of the press.; and the term bp is due to the formation of PtI_2 by the attack of the phosphorus layer by iodine atoms at a rate proportional to the press. of the iodine vapour. The rate of formation of PtI_2 rapidly becomes negligible in comparison with that of PtI. Below a certain critical press. the surface of the metal is bare, and the formation of PtI becomes a reaction of the first order. The reaction was studied by L. Jacobs and H. K. Whalley, C. Nogareda, G. E. Pringle and G. van Praagh, and G. van Praagh. L. Wöhler, and C. Engler

and L. Wöhler noted that a small quantity of iodine is absorbed by platinum black from $0{\cdot}01N$-soln. of iodine. W. R. Hodgkinson and F. K. S. Lowndes observed that with a red-hot platinum wire in the vapour of **iodine chloride,** platinous chloride, and traces of the iodide are formed. W. Engelhardt found no action occurs between colloidal platinum and iodine. W. Pullinger observed that platinum is attacked by a soln. of iodine. For G. Gore's observations on the action of iodine and silver fluoride, *vide supra.* M. Bodenstein and V. Meyer noted the union of hydrogen and iodine is favoured by hot platinized asbestos. C. N. Hinshelwood and R. E. Burk, and A. Oelander studied the decomposition of hydrogen iodide on a platinum surface. H. St. C. Deville observed that **hydriodic acid** has virtually no action on platinum, and W. Pullinger found that platinum sponge dissolves in hydriodic acid to form platinic iodide. According to C. F. Schönbein, a soln. of hydriodic acid, or an acidic soln. of **potassium iodide,** liberates iodine in the presence of platinous black, but not so with neutral soln. of potassium iodide; on the other hand, L. Wöhler observed that in air, on a water-bath, iodine is slowly liberated by platinum black from a neutral soln. of potassium iodide. The platinum black loses this property if it has been preheated to a high temp. If the platinum black is freed from occluded gases it has no action on soln. of potassium iodide, but it becomes active if it be exposed to air anew. W. Skey noted that platinum loses its power of liberating iodide from potassium iodide soln. by calcination, or by washing with ammonia or alkaline soln., and it becomes active again if it be exposed to air, or digested with hydrochloric or sulphuric acid—hot or cold. G. Just observed that platinum foil which has been dipped in a soln. of potassium ferricyanide and thoroughly washed, can liberate iodine from a soln. of potassium iodide. H. Danneel observed that if a soln. of hydriodic acid be shaken with finely-divided platinum and silver, in an atmosphere of hydrogen, silver iodide is formed. The reaction is reversible. H. S. Taylor studied the decomposition of potassium iodide on platinum surfaces. A. Connell observed that **iodic acid** has no action on platinum, and C. F. Schönbein found that a soln. of indigo-blue is decolorized by iodic acid or by a soln. of **potassium iodate** in the presence of platinum black at ordinary temp., and O. Loew and K. Aso, that potassium iodate is reduced to iodide by glucose and platinum black. G. Lemoine studied the catalytic effect of platinum on the reaction between iodic and oxalic acids. E. Schaer noted that the oxidation of some organic substances by the iodates is favoured by the presence of colloidal platinum.

There are two groups of catalyzed reactions: I. **Homogeneous catalysis** in which the catalyst is not separated by a boundary surface from the reacting mixture—*e.g.* water vapour in the oxidation of carbon monoxide; and of hydrochloric acid in the hydrolysis of ethyl acetate. II. **Heterogeneous catalysis** in which the catalyst exposes a boundary surface to the reacting mixture—*e.g.* in the **contact catalysis** of manganese dioxide in the decomposition of potassium chlorate, there is a solid-solid boundary surface; with platinum in the oxidation of sulphur dioxide there is a gas-solid boundary surface; and with mercury in the decomposition of hydrogen peroxide, there is a liquid-liquid boundary surface. There are two main explanations of the way heterogeneous catalysts do their work:

(i) *The intermediate compound theory* exemplified by the so-called **chain reactions,** or **cyclic reactions.** Thus, J. Mercer (1842) attributed the action of manganese dioxide on potassium chlorate to the cycle with Mn_2O_7 as the intermediate compound; similarly, T. Fleitmann (1865), the effect of cobalt salts on the production of oxygen from hypochlorites to the alternate formation and decomposition of a higher cobalt oxide; A. de la Rive (1834), and C. Engler (1901), the action of platinum on the union of hydrogen and oxygen which is taken to involve the formation of superficial films of oxide in the cyclic reactions: $2Pt+O_2=2PtO$, followed by $PtO+H_2=Pt+H_2O$; and G. Bredig and A. von Antropoff (1906), the effect of mercury on the decomposition of hydrogen peroxide to the formation of mercury peroxide as an intermediate compound.

(ii) *The condensed film or adsorption theory*, exemplified by the so-called **wall-reactions**, was suggested by M. Faraday (1833), in which the gases—say hydrogen and oxygen—are condensed on the surface of the catalyst; and it is assumed that under the pressure due to surface forces the gases can react more rapidly since it is known that high pressures usually augment the reactivity of gases. Thus, N. Beketoff (1859), and W. Ipatéeff (1909), have shown that hydrogen gas under high pressures can displace silver and several other metals from solutions of their salts.

T. Graham (1868) thought it possible that when a metal adsorbs a film of gas, the gas molecules are orientated in such a way that the same parts of the molecules are all in direct contact with the metal, and the other parts are exposed to the gas. According to I. Langmuir (1916), the adsorbed layer is unimolecular in thickness, and generally orientated. The poisoning of a solid catalyst is then due to the formation of films of molecules of the "poison gas" on the catalyst, which prevent the adsorption of gases which would otherwise react on the surface of the catalyst. The adsorbed molecules are held by attractive forces analogous to residual affinity, for a molecule in the interior of a liquid or solid is attracted by other molecules equally in all directions, whereas a molecule on the surface can be attracted inwards by the other molecules. Accordingly, the surface molecules of a solid or liquid are supposed to exert a residual, uncompensated attraction. When gases are adsorbed by the crystals of a salt, F. Haber (1914) attributed the attraction to the electrical forces produced by the positively and negatively charged ions at the surfaces of the crystals. The adsorption theory of catalysis assumes many forms. In general, it is supposed that under certain conditions, when molecules are adsorbed on the surface of the catalyst, they are activated in some way so that chemical change may occur more favourably. The force of adsorption is thus related to chemical forces, for the **activation of the molecules** by the catalyst is attributed to the lowering of the energy required to break down the molecules of the reacting substances by distorting, dislocating, straining, or profoundly modifying the adsorbed molecules. Hence, (i), in the so-called *molecular distortion theory*, the affinity is supposed to be weakened by the adsorption forces so that the atoms of the molecule are loosened or partially separated; and (ii), in the *atomic distortion theory*, the affinity is supposed to be weakened by the disturbing effect of the catalyst on the intra-atomic, electronic orbits of the atoms.

The adsorption of one or both the reacting gases by the catalyst may occur in different ways—*e.g.* a diatomic gas may be adsorbed so that it forms a molecular or an atomic layer or both. The molecular distortion may mean that the molecule is attached (adsorbed) at more than one point on the catalyst, so that the molecule is stretched, twisted, or otherwise strained, and, in consequence, becomes less stable, *i.e.* chemically activated—*multiple adsorption* theory. H. Andrews (1930) suggested that the adsorbed molecules, in the unimolecular adsorption film on the surface of the catalyst, may be so attached that only one of their atoms is linked to the catalyst. As a result, the distribution of the intramolecular vibrational energy will be so changed that it possibly accumulates on one particular bond, which thus becomes weakened, and, in consequence, activated. Again, according to H. S. Taylor (1925), the activity of the catalyst may be confined to a certain number of adsorption centres. The fact that the catalyst in some cases is active only when finely-divided, and when prepared at a low temperature, may mean that some of the atoms have not attained the orderly arrangement possessed by the crystal lattice. The vagabond atoms of the catalyst, left out of the lattice structure, will have a different adsorptive power for the reacting gases, and the localities where these atoms occur may be special centres of adsorption and, consequently, of catalytic activity. M. Bodenstein (1929) suggested that the rate of the catalytic reaction may be determined by the speed at which one of the reacting substances moves through the unimolecular adsorption film of gas to the centres of activity on the catalyst.

A catalyst may exert a very specific action so that **the catalyst directs the reaction in one direction in preference to another.** This is exemplified by P. Sabatier's work on the catalysis of organic compounds. Thus, the vapour of formic acid is decomposed into hydrogen and carbon dioxide when passed over zinc oxide, and into water and carbon monoxide when passed over titanic oxide:

$$H.COOH\begin{cases} ZnO & \rightarrow H_2+CO_2 \\ TiO_2 & \rightarrow H_2O+CO \end{cases}$$

Ethyl alcohol in the presence of nickel decomposes into acetaldehyde and hydrogen; and in the presence of alumina, it forms ethylene and water:

$$C_2H_5OH\begin{cases} Ni & \rightarrow CH_3.COH+H_2 \\ Al_2O_3 & \rightarrow C_2H_4+H_2O \end{cases}$$

Again, a mixture of carbon monoxide and hydrogen, at 300°, furnishes chiefly formaldehyde in the presence of copper at 300°; chiefly methyl alcohol in the presence of a mixture of zinc and chromium oxides at 300° to 358°; and chiefly methane in the presence of finely-divided nickel at 150° to 200°:

$$CO+nH_2\begin{cases} Cu & \rightarrow H.COH \\ Cr_2O_3 & \rightarrow CH_3OH \\ Ni & \rightarrow CH_4+H_2O \end{cases}$$

Again, the presence of water vapour *favours* the oxidation of carbon monoxide; the union of hydrogen and oxygen; the union of the hydrogen and chlorine; and the union of hydrogen chloride and ammonia. In fact, if these gases be intensely dried, the reactions may not occur under conditions where the moist gases readily combine. The catalyst is here supposed to act by a cycle or chain of reactions, say: $CO+H_2O=CO_2+H_2$; followed by: $2H_2+O_2=2H_2O$. At high temperatures, the reaction: $2CO+O_2=2CO_2$, may proceed directly. On the other hand, a catalyst may retard the progress of a reaction, and it is then called a **negative catalyst.** Thus, K. Than (1864) found that the presence of water vapour *retards* the decomposition of ammonia; W. A. Shenstone (1887), that dry ozone at 0° decomposes 30 times as rapidly as the moist gas at 26·4°; and H. G. van de Stadt (1893), that moisture retards the oxidation of phosphorus.

The presence of certain impurities may reduce the chemical activity of the catalyst resulting in what is metaphorically called a **poisoning of the catalyst.** E. Turner (1823), M. Faraday (1834), and W. C. Henry (1836), for example, noticed that finely-divided platinum becomes less active in stimulating the reaction between hydrogen and oxygen if certain foreign gases are present—the presence of carbon monoxide, and ethylene act as **inhibitors** of the reaction. Again, the oxidation of sulphur dioxide in the presence of a catalyst was not successful commercially until it was found that the reacting gases must first be freed from arsenical compounds which poison the catalyst; sulphur compounds also act as poisons in the synthesis of ammonia, and in hydrogenation processes. The poison is thought to act by being preferentially adsorbed on the surface of the catalyst.

In some cases, the activity of a catalyst is enhanced by admixture with another catalyst so that the activity of the mixture is greater than the sum of the activities of the individual constituents. This is the so-called **promotor action.** For example, dehydrating agents act as promotors in the catalytic hydrogenation of carbon monoxide or dioxide. Finely-divided manganese oxide favours the oxidation of carbon monoxide at temperatures as low as —30°, but the catalyst is poisoned by alkali, and promoted by cupric oxide. The catalyst called *hopcalite* is manganese and cupric oxides in the proportions 3 : 2. The poisoning by alkali does not occur so readily with the promoted catalyst. In some cases the promotor acts by increasing the available catalytic surface; or by reducing the tendency of the catalyst to sinter by heat. The promotor may also favour the decomposition of the inter-

mediate compound formed by the catalyst, or the catalyst may favour the decomposition of the intermediate compound formed by the promotor.

A. Orlowsky[13] found that the affinity of **sulphur** for platinum is quite small. C. Ridolfi observed that no sulphide is formed by the direct action of sulphur. E. Davy observed that some platinum sulphide is formed when the metal is heated with sulphur; and G. Preuner observed that the action is not particularly strong even between 950° and 1240°. A. Wigand found that the metal acquires a dark brown film in boiling sulphur. W. C. Heraeus and W. Geibel, and W. R. Hodgkinson and F. K. S. Lowndes, observed that sulphur vapour had no perceptible action on an electrically heated platinum wire. A. Jedele observed that sulphur has a limited solubility in platinum, and that the effect of sulphur on the yield point and fracture, in kgrms. per sq. mm., and the percentage elongation at room temp., and at 850°, are indicated in Table II. J. Milbauer found that platinum

TABLE II.—THE EFFECT OF SULPHUR ON THE TENACITY OF PLATINUM.

S per cent.	Room temperature			850°		
	Yield	Fracture	Elongation	Yield	Fracture	Elongation
0·15	12·7	19·9	14·7	6·4	8·7	5·8
0·06	11·2	16·6	10·1	6·1	6·9	5·5
0·02	9·9	16·3	26·2	5·3	7·4	14·0
0·006	9·4	15·3	24·7	4·3	5·3	14·5

black accelerates catalytically the formation of hydrogen sulphide by passing hydrogen over molten sulphur at 278°; and Y. Venkataramaiah observed that hydrogen which has diffused through platinum will attack sulphur. According to R. Böttger, if gun-cotton be impregnated with platinum black, it detonates immediately when exposed to **hydrogen sulphide.** E. B. Maxted noted that the presence of hydrogen sulphide retards the adsorption of hydrogen by platinum. The gas is strongly adsorbed by platinum, and on degassing the metal at 100°, an equal vol. of hydrogen is evolved, the sulphur remaining on the platinum. Both before, and to a smaller extent after this treatment, the rate of adsorption of hydrogen by platinum is markedly retarded, but there is no decrease in the ultimate proportion of gas adsorbed. W. Skey noted that the surface of platinum is altered by exposure to hydrogen sulphide, or **ammonium sulphide,** so that the metal no longer amalgamates with mercury. M. Domanicky said that the attack by **sulphur monochloride** is very slow if at all. According to W. R. Hodgkinson and F. K. S. Lowndes, **sulphur dioxide** has no action on an electrically heated platinum wire. J. Uhl observed that sulphur dioxide acts on platinum, producing platinum sulphide and sulphur trioxide. E. Mulder noted the action of sulphur dioxide in a gas-flame on platinum crucibles. A. Sieverts and E. Jurisch noted that sulphur dioxide is insoluble in compact platinum; but G. Magnus said that at 0° platinum absorbs about one-third of its vol. of sulphur dioxide. J. P. Cooke and T. W. Richards, D. O. Shiels, and D. Tommasi also noted that some sulphur dioxide is absorbed by platinum. P. Chappuis measured the heat developed when platinum black absorbs sulphur dioxide; and G. B. Taylor and co-workers gave approximately 25,000 cals. for the heat of adsorption. The subject was studied by B. Neumann and E. Goebel. The oxidation of sulphur dioxide by air or oxygen in the presence of spongy platinum or platinum black was discussed by I. E. Adaduroff and co-workers, T. von Artner, Badische Anilin- und Sodafabrik, E. Baur, M. Bodenstein and co-workers, G. Bodländer and K. von Köppen, M. O. Charmandarian and G. D. Dachniuk, Chemische Fabrik vorm. Goldenberg und Geromont, C. L. Clark and co-workers, P. D. Dankoff and co-workers, J. W. Döbereiner, L. Duparc and co-workers, O. Efrem, Farbwerke vorm.

Meister, Lucius und Brüning, W. Grillo and M. Schröder, E. de Haën, E. Hänisch and M. Schröder, H. N. Holmes and co-workers, J. T. Jullion, R. Knietsch, K. von Köppen, G. R. Levi, G. R. Levi and M. Faldini, G. Magnus, E. B. Maxted and A. N. Dunsby, R. Messel and W. S. Squire, H. Neuendorf, B. Neumann and H. Jüttner, S. Pastorelli, J. H. Perry, P. Phillips, E. Raynaud and L. Pierron, C. L. Reese, E. S. Ridler, E. J. Russell and N. Smith, C. F. Schönbein, D. O. Shiels, A. Skrabal, G. C. Stone, J. S. Streicher, G. B. Taylor and S. Lenher, A. P. Thompson, W. H. Thornthwaite, A. Trueman, C. Winkler, F. Winteler, and L. Wöhler and co-workers. I. E. Adaduroff and K. I. Brodovitsch investigated carriers of the platinum—*e.g.* asbestos, and silica gel; G. L. Clark and co-workers observed no activation of the catalyst by X-rays; but R. Schwarz and M. Klingenfuss noted an acceleration; and E. B. Maxted and A. N. Dunsby studied the poisoning of the platinum by arsenic; and G. R. Levi and M. Faldini, the deleterious effect of iridium and rhodium—*vide* **10**. 57, 27. E. Mulder found that platinum black favours the oxidation of **sulphurous acid**; L. Wöhler noted that sulphurous acid dissolves a little platinum black; and J. H. Gladstone, that platinum black charged with hydrogen reduces sulphurous acid to hydrogen sulphide. C. Geitner showed that finely-divided platinum does not hinder the decomposition of sulphurous acid at an elevated temperature; but sulphurous acid decolorizes soln. of platinic chloride. Platinic chloride in a sealed tube with sulphurous acid at 200° forms platinous sulphide. A. Hantzsch found that spongy platinum decomposes **potassium nitrosyl sulphite** into potassium sulphate and nitrous oxide; and similarly also with **ammonium nitrosyl sulphite.** H. B. North found that platinum is not attacked by **sulphuryl chloride** in a sealed tube at ordinary temp.; and there is a very slight corrosion after many hours' exposure at 150°, but after many days' heating at this temp., crystals of platinic chloride are formed.

H. St. C. Deville and J. S. Stas observed that platinum black, precipitated by formic acid, is fairly soluble in boiling **sulphuric acid,** and M. Delépine, that some platinum vessels are attacked by boiling sulphuric acid, whilst others are not attacked unless the acid contains nitrous fumes in soln. According to F. C. Carter, platinum is attacked by hot sulphuric acid but not by the cold acid. A. Scheurer-Kestner showed that the dissolution of platinum in boiling sulphuric acid is a true solution process, and is not dependent on oxidation. Under similar conditions, 93 to 94 per cent. sulphuric acid dissolved a gram of platinum per 1000 kgrms.; 98 per cent. sulphuric acid dissolved 6 to 7 grms. of platinum per 1000 kgrms.; and 99 per cent. sulphuric acid dissolved 9 grms. of platinum per 1000 kgrms. The solubility was greater if the sulphuric acid contained nitrous fumes in soln.; and if the metal was alloyed with iridium, the resistance to attack was greater. E. Hartmann and F. Benker discussed this subject. C. Marie observed that the presence of potassium sulphate accelerates the attack by sulphuric acid; L. R. W. McCay, that the presence of sulphurous acid or of antimony trioxide or arsenic trioxide, retards the attack; and A. H. Allen, that sulphuric acid containing potassium permanganate does not attack platinum. Owing to the reducing action of ammonium sulphate, M. Delépine found that platinum does not lose weight when boiled in sulphuric acid containing ammonium compounds, and the contrary result by J. T. Conroy was obtained at a lower temp. The reducing action is symbolized: $4H_2SO_4+Pt=Pt(SO_4)_2+2SO_2+4H_2O$; and $3Pt(SO_4)_2+2(NH_4)_2SO_4=2N_2+3Pt+8H_2SO_4$. L. Wöhler found that dil. sulphuric acid dissolves the minutest trace of platinum black, but leaves spongy platinum untouched; W. C. Heraeus gave for the solubility of platinum in 94 per cent. acid, 0·6 grm. per ton, and in 97 per cent. acid, 2·0 grms. per ton. The time the metal is exposed to the acid and the surface area of the metal should be stated. J. T. Conroy found that in 28 hrs. 0·04 grm. was dissolved by 95 per cent. sulphuric acid at 250° to 260°. R. H. Adie observed no formation of sulphur dioxide or hydrogen sulphide with warm (200°) or cold, conc. sulphuric acid. According to M. Delépine, 1 sq. dm. of platinum foil, 10μ to 20μ thick, during an hour's

exposure to sulphuric acid containing potassium sulphate lost weight at the rate of 0·008 to 0·012 grm. per hour. At 350° to 355°, and a mixture of 50 grms. sulphuric acid and 10 grms. of potassium sulphate, the loss is 0·04 to 0·05 grm.; and with a mixture of 50 grms. of sulphuric acid and 20 grms. of potassium sulphate, the loss at 365° to 370° amounted to 0·12 to 0·13 grm. With sulphuric acid containing in soln.

Nitric acid	0	0·00002	0·00004	0·0001	0·001 part
Loss in weight	0·0088	0·0075	0·0118	0·0083	0·0080 grm.

so that the effect is very small. R. H. Adie observed no evolution of hydrogen sulphide or sulphur dioxide at 250°. The subject was studied by G. J. Burch and J. W. Dodgson. L. Quennessen found that sulphuric acid, containing 94 per cent. H_2SO_4 and free from nitrous acid, has very little solvent action on platinum when the two are heated in a vacuum at 400°, but in the presence of oxygen the platinum is dissolved and the oxygen absorbed, whilst sulphuric acid containing a slight excess of sulphur trioxide in soln. dissolves platinum at 400° in vacuo to the same extent as the more dilute acid in the presence of oxygen. Expressing solubilities in grams of metal dissolved per sq. decimetre per hour, 94 per cent. sulphuric acid, and commercial platinum 0·001 grm. in vacuo, and 0·124 grm. in oxygen; with purified platinum, the data were, respectively, 0·0006 and 0·0227 grm.; and sulphuric acid with 2 per cent. of free sulphur trioxide dissolves 0·0265 grm. of platinum in vacuo. E. Salkowsky observed no acceleration in the attack by dil. sulphuric acid in the presence of hydrogen dioxide. K. W. Frölich observed that whilst platinum is rarer than gold when it is in contact with sulphuric acid at ordinary temp., the case is reversed above 200°, as illustrated in Fig. 28, which gives the e.m.f. of the millivolts against the $Hg_2Cl_2|Hg$ electrode at different temp. H. St. C. Deville and H. Debray observed that cast platinum vessels resist boiling sulphuric acid better than those made from malleable platinum. When an alloy of platinum and zinc is treated with sulphuric acid, C. Gourdon found that some platinum passes into soln. with the zinc. H. Debray observed that the presence of platinum hastens the dissolution of tin, lead, or zinc in acids —*vide supra*. J. H. Gladstone and A. Tribe found that platinum containing occluded hydrogen furnishes sulphur dioxide when it is treated with sulphuric acid; S. Cooke, that conc. sulphuric acid slowly yields sulphur dioxide when it is treated with hydrogen in the presence of platinum; and J. Milbauer, that the presence of platinum retards the accelerated formation of sulphur dioxide produced by the presence of mercuric sulphate in sulphuric acid treated with hydrogen. The catalytic action of platinum is poisoned by arsenic trioxide. F. C. Carter noted that platinum is attacked by fused **potassium hydrosulphate,** $KHSO_4$. M. G. Levi and E. Migliorini observed that platinum black acts on **ammonium sulphate** to form some nitric acid—*vide infra*. C. J. Thatcher studied the effect of platinum on the electro-oxidation of **sodium thiosulphate** to tetrathionate. M. G. Levi and E. Migliorini found that platinum black accelerates the decomposition of **persulphates** of ammonium, potassium, and sodium; smooth platinum is inactive. T. S. Price observed that colloidal platinum does not decompose soln. of potassium or ammonium persulphate, or of **perdisulphuric acid.** J. A. N. Friend represented the reaction: $K_2S_2O_8+H_2O_2=K_2SO_4+H_2SO_4+O_2$. C. Marie observed that an acidic soln. of potassium persulphate slowly attacks platinum. T. S. Price found **permonosulphuric acid** is decomposed slowly by platinum, and rapidly if hydrogen dioxide be present. The reaction was studied by L. Wöhler. T. S. Price and

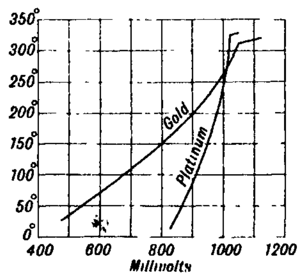

FIG. 28.—The Electromotive Force of Platinum and Gold in Concentrated Sulphuric Acid at Different Temperatures.

J. A. N. Friend represented the reaction: $H_2SO_5+H_2O_2=H_2SO_4+H_2O+O_2$. M. Traube found that platinum black hinders the formation of persulphuric acid by the electrolysis of 40 per cent. sulphuric acid; and G. Petrenko studied the effect of the platinum electrodes on the yield of persulphuric acid. M. G. Levy and co-workers studied the reaction with soln. of **potassium persulphate.**

J. J. Berzelius,[14] and F. Rössler observed that when **selenium** is heated with spongy platinum, union occurs with vivid combustion and a selenide is formed. A. Orlowsky studied the affinity of platinum for sulphur and selenium. R. Marc found that platinum favours the production of the high conductivity form of selenium exposed to light. E. Mitscherlich found platinum to be insoluble in **selenic acid.** F. Rössler showed that finely-divided platinum and **tellurium** unite with incandescence when heated to form a telluride. J. W. Mellor noted that platinum crucibles are attacked by some **selenides.**

According to R. Vondracek,[15] platinum black in a soln. of ammonia takes up **nitrogen,** which can be driven from the metal by treatment with potash-lye. S. H. Bastow, J. C. Stimson, and G. I. Finch and J. C. Stimson studied the subject. W. W. Randall said that nitrogen does not diffuse through heated platinum. E. J. B. Willey studied the activation of nitrogen in the presence of platinum. F. Wolfers found that nitrogen in the presence of nickel forms nickel nitride, which then attacks the platinum between 300° and 600°, and makes the metal brittle. H. Damianovich and G. Berraz studied the action of nitrogen at a low press. and exposed to an electric discharge. B. Delachanal observed that commercial platinum occludes 0·36 to 0·91 c.c. of nitrogen per 100 grms. of metal; H. Dobretsberger, the effect of absorbed nitrogen on the high-frequency resistance of platinum; A. Féry, the effect of nitrogen on the electrical resistance; and H. Damianovich, the action on the rate of dissolution in aqua regia. S. H. Bastow said that in the absorption of nitrogen by films of platinum, where the metal is presumed to be in the atomic state of subdivision, as the temp. is raised, the nitrogen is given off. The adsorbed nitrogen reacts with hydrogen or water to form ammonia, so that it is assumed that PtN_2 is formed. F. Wolfers observed that nitrogen acts on platinum in the presence of nickel, presumably a volatile nickel nitride is formed at about 300°, and that then attacks platinum at 600° making it brittle. Hence nickel-platinum thermocouples should not be used above 500°. L. Wöhler, O. Loew, and E. J. Russell and N. Smith discussed the oxidation of atm. nitrogen in air in the presence of alkaline soln. and platinum black to form nitrous acid or ammonium nitrite. G. T. Beilby and G. G. Henderson found that if platinum be heated in **ammonia** to 800°, the surface of the metal is darkened, and dulled, and under the microscope has a bubbly appearance. The surface film can be rubbed off with filter paper; the frictional electricity of the metal is reduced; and the electrical resistance is increased. W. C. Heraeus observed no perceptible change in a platinum wire heated in ammonia for half an hour at 1500°. The formation of ammonia by passing a mixture of hydrogen and nitrogen over spongy platinum at a dull red-heat, and in other ways, was discussed by L. Brunel and P. Woog, J. K. Dixon, G. S. Johnson, P. Jolibois and F. Olmer, F. Kuhlmann, O. Loew, W. Nernst and F. Jost, H. S. Taylor, L. Wöhler, L. T. Wright, and J. Y. Yee and P. H. Emmett—*vide* **8.** 49, 15; the retarding or poisoning effects of acetylene, phosphine, and hydrogen sulphide were studied by J. Y. Yee and P. H. Emmett; the oxidation of ammonia by the action of oxygen in the presence of spongy platinum or platinum black, by L. E. Adaduroff and co-workers, E. A. Arnold and R. E. Burk, V. I. Atroshchenko, G. T. Beilby and G. G. Henderson, A. K. Brewer, E. Decarrière, J. W. Döbereiner, L. Duparc and co-workers, W. Frankenberger and co-workers, S. L. Handforth and J. N. Tilley, W. Hennel, W. Henry, A. Klages, K. Kraut, A. Luyckx, D. Meneghini, L. Mond and co-workers, A. A. Noyes and G. V. Sammet, W. Ostwald and E. Bauer, J. R. Partington, P. Pascal and E. Decarriere, N. A. Figurovsky, W. Reinders and A. Cats, O. Schmidt and R. Böcker, C. F. Schönbein,

G. M. Schwab and H. Schmidt, A. Trillat, S. Uchida, R. Vondracek, H. W. Webb, and H. C. Woltereck—*vide* **8**. 49, 18; the formation of ammonia from nitric acid and alcohol in the presence of platinum black, by J. W. Döbereiner; W. Skey noted that aq. ammonia affects the surface of platinum so that it cannot be amalgamated with mercury until it has been treated with an acid. R. E. Burk examined the effect of platinum on the thermal decomposition of ammonia. R. Coustal and H. Spindler found that a platinum anode is slowly attacked in liquid ammonia. The decomposition of **hydrazoic acid** by platinum as catalyst was studied by E. Oliveri-Mandala. The decomposition of **hydrazine,** $2N_2H_4=2NH_3+N_2+H_2$, and $3N_2H_4=2NH_3+2N_2+3H_2$, with platinum black as catalyst was studied by A. Gutbier and K. Neundlinger, K. Neundlinger, and E. Oliveri-Mandala. A. Purgotti and L. Zanichelli found that platinum freed from air would not endure the decomposition of hydrazine, whilst ordinary platinum preparations will do so, but the deaerated platinum will endure the decomposition of hydrogen dioxide, and of hydroxylamine. The decomposition of **hydrazine sulphate** with platinum as a catalyst was studied by S. Tanatar; and the oxidation of hydrazine, $N_2H_4+O_2=2H_2O+N_2$, by A. Purgotti and L. Zanichelli. The reduction of **hydroxylamine** to ammonia in the presence of finely-divided platinum: $4NH_2OH=2NH_3+N_2O+3H_2O$, was studied by V. Meyer, A. Findlay and W. Thomas, O. Loew, O. Flaschner, E. Oliveri-Mandala, and S. Tanatar.

H. Cassel and E. Glückauf,[16] and J. Lüke and R. Fricke observed that **nitrous oxide** has no action on glowing platinum; J. Lüke and R. Fricke found that the nitrous oxide is decomposed. E. W. R. Steacie and J. W. McCubbin, G. M. Schwab and B. Eberle, J. K. Dixon and J. E. Vance, M. S. Shah, J. A. Hedvall and co-workers, G. van Praagh and B. Topley, and C. N. Hinshelwood and C. R. Prichard studied the effect of platinum on the thermal decomposition of nitrous oxide; L. Duparc and co-workers, the hydrogenation of this oxide with platinum as catalyst; and M. L. Nichols and I. A. Derbigny, the reduction of the oxide by titanous chloride. W. R. Hodgkinson and F. K. S. Lowndes could not detect any action when a red-hot platinum wire is exposed to **nitric oxide.** L. Duparc and co-workers studied the hydrogenation of nitric oxide with platinum as catalyst; and J. Zawadzky and co-workers, the decomposition of nitric oxide. P. Sabatier and J. B. Senderens did not observe any oxidation of platinum by **nitrogen peroxide.** G. B. Taylor and co-workers studied the hydrogenation of nitric oxide in the presence of platinum; and T. E. Green and C. N. Hinshelwood, the decomposition of the gas by hot platinum wire. L. I. de N. Ilosva observed that when air is passed over platinum wire at 280° to 350°, spongy platinum at 250° to 350°, or platinum black at 180° to 300°, nitrogen trioxide is formed. The oxidation of nitrogen with heated platinum as catalyst was studied by O. Dieffenbach and W. Moldenhauer, K. Kaiser, O. Loew, D. R. Lovejoy, and L. Wöhler; the catalytic action of platinum on the decomposition of nitric oxide, by J. L. Gay Lussac, M. Berthelot, F. Emich, K. Jellinek, and P. Sabatier and J. B. Senderens—*vide* **8**. 49, 35; and the reduction of nitrogen oxides by hydrogen with platinum as catalyst, by S. Cooke, A. Jouve, and the Wertdeutsche Thomasphosphatwerke. J. J. Sudborough found that **nitrosyl chloride** does not attack platinum in the cold, but at 100°, $PtCl_4.2NOCl$ is slowly formed. L. Wöhler observed that **nitrous acid** free from chlorides does not dissolve platinum black. The reduction of nitrous acid, and of **alkali and ammonium nitrites,** by platinum black was studied by A. A. Blanchard, S. Cooke, O. Flaschner, O. Loew, J. Meyer and E. Trützner, and H. N. Warren. R. Vondracek suggested that the decomposition of ammonium nitrite by platinum black proceeds in two stages: firstly, the platinum black, which, to begin with, contains oxygen, oxidizes the ammonium nitrite, thus: $2NH_4NO_2+xPtO_n+yH_2O=N_2+2HNO_2+xPt+(y+3)H_2O$, and, secondly, the nitrous acid formed in the first stage is reduced by the platinum, which is now oxygen-free, thus: $2nHNO_2+xPt=nN_2+nH_2O+Pt_xO_n$. L. Wöhler found that **nitric acid** does not dissolve platinum black. C. Marie observed that warm, conc.

nitric acid slowly attacks platinum, and F. M. Gavriloff studied the solubility of platinum alloyed with silver in this acid. T. Gross noted that platinum is attacked when a mixture of sulphuric and nitric acids is subjected to an alternating current in a platinum crucible. The reduction of nitric acid, and of **alkali and ammonium nitrates,** was studied by S. Cooke, J. H. Gladstone, J. H. Kastle and E. Elvove, O. Loew, O. Loew and K. Aso, and C. F. Schönbein; whilst F. C. Carter, and G. P. Baxter and F. L. Grover added that the purified metal is not attacked by hot conc. nitric acid; and fused alkali nitrates do not attack the metal. C. Fromme studied the electrochemical behaviour of nitric acid towards platinum—*vide* Grove's cell. C. Marie, and J. Jannek and J. Meyer observed that hot, conc. nitric acid, not the fuming acid, has a distinct action on platinum; and J. H. Gladstone and A. Tribe noted that ordinary nitric acid has no action on platinum, with platinum containing occluded hydrogen, the hydrogen is turbulently oxidized. C. Winkler observed that platinum dissolves in purified nitric acid only when the metal is alloyed with other metals like copper, silver, gold, lead, and bismuth; and N. Tarugi observed that platinum is more or less soluble in nitric acid when mercury is present. E. Schaer showed that the oxidation of some organic substances by nitric acid and the nitrates is favoured by the presence of colloidal platinum. C. Bromeis found that electroplated films of platinum—$\frac{1}{3000}$th line thick—resist the strongest acids; C. Kellner observed that acids are adsorbed by platinum black; and O. Loew and K. Aso noted that the reduction of nitric acid to ammonia in the presence of dextrose and platinum black. S. J. Green studied the reduction of nitric compounds.

According to H. Bornträger, platinum dissolves in **aqua regia** with an excess of hydrochloric acid to form hydrochloroplatinic acid, and with an excess of nitric acid, to form platinic nitrosyltetrachloride. Similar results were obtained with mixtures of nitric and hydrobromic acids. T. A. Edison discussed the action of aqua regia on platinum. N. A. E. Millon observed that the metal does not dissolve in aqua regia if no nitrous acid is present—*vide infra,* hydrochloroplatinic acid—and if the aqua regia contains a large proportion of a potassium salt, the attack is greatly retarded. H. Dullo found that the attack is accelerated under press. A. Muckle and F. Wöhler found that aqua regia does not dissolve all the platinum from an iridium-platinum alloy—much remains associated with undissolved iridium; and J. W. Mallet also observed that platinum-iridium alloys strongly resist the action of aqua regia. C. Claus found that of the platinum metals, palladium dissolves most readily in aqua regia and platinum comes next. The other metals in a compact state do not dissolve in this acid. C. Reinhardt said that in these cases it is best to alloy the metal with zinc, digest the alloy in cold hydrochloric acid of sp. gr. 1·142, and dissolve the residue in aqua regia.

According to E. Davy,[17] **phosphorus** combines with spongy platinum in an evacuated tube considerably below a red-heat; the union is attended by flame and vivid incandescence, and platinum phosphide is formed which F. W. Clarke and O. T. Joslin represent by Pt_3P_5. A. Granger observed that the vapour of phosphorus attacks finely-divided platinum at 500°; W. C. Heraeus gave 600° for the temp. of formation of phosphide with compact platinum; and W. R. Hodgkinson and F. K. S. Lowndes found that a red-hot platinum wire is immediately destroyed by phosphorus vapour. W. Biltz and co-workers studied the equilibrium diagram, with the compounds PtP_2 and $Pt_{20}P_7$. A. Jedele observed that the platinum phosphides—Pt_2P, PtP, and Pt_3P_5—are very sparingly soluble in the metal, and the effect of phosphorus on the yield point and fracture in kgrms. per sq. mm., and the percentage elongation at room temp., and at 850° are indicated in Table III. H. W. Melville and E. B. Ludlam studied the catalytic effect of platinum on the oxidation of phosphorus. H. le Chatelier noted that platinum thermocouples are spoilt by the vapours of phosphorus. C. F. Schönbein found platinum black makes dry phosphorus at −5° luminesce; and H. W. Melville and E. B. Ludlam studied the catalytic oxidation of the vapour of phosphorus by plati-

num at 200°. O. J. Walker observed that in the precipitation of copper or silver from soln. of their salts by phosphorus, if a conducting metal like platinum be in contact with the phosphorus, the silver or copper is deposited on the platinum. H. Moissan observed that when **phosphorus trifluoride or pentafluoride** is passed over red-hot spongy platinum, some **platinous phosphopentafluoride,** $PtF_2.PF_3$, and phosphide are formed. E. Baudrimont found that spongy platinum and **phosphorus trichloride** at 250° form a platinum chloride; J. H. Gladstone said that the compact metal is not attacked. W. R. Hodgkinson and F. K. S. Lowndes found that a red-hot platinum wire in the vapour of **phosphorus pentachloride** produces a flame, some phosphorus is formed, and this reacts with the metal, forming a fusible phosphide. According to E. Baudrimont, phosphorus pentachloride, at 200°, attacks the metal, and at a higher temp., a volatile compound of platinic and phosphoric chlorides is formed. The subject was also studied by P. Schützenberger, and P. Schützenberger and M. Fontaine. H. Goldschmidt

TABLE III.—THE EFFECT OF PHOSPHORUS ON THE TENACITY OF PLATINUM.

P per cent.	Room temperatures			850°		
	Yield	Fracture	Elongation	Yield	Fracture	Elongation
0·26	21·4	25·9	4·75	—	—	—
0·105	16·8	23·5	11·3	—	—	—
0·025	16·3	21·4	19·4	—	—	—
0·005	13·9	20·9	11·9	—	—	—
0·003	10·4	13·9	14·2	3·6	4·2	6·2
0·001	12·2	14·9	24·9	6·2	7·9	6·1
0·000	8·7	14·8	27·1	5·1	6·9	9·0

represented the reaction with compact platinum $PCl_5+Pt=PCl_3+PtCl_2$. W. Ramsay and J. Shields observed that no hydrogen is liberated by boiling platinum black with a soln. of **sodium hypophosphite** owing to the oxygen occluded by the metal. The reaction was studied by A. Sieverts, and M. Major. A. Sieverts observed that platinum black is a catalyst for the oxidation of the hypophosphite. A. A. Vedensky and A. V. Frost found that colloidal platinum favours the oxidation of **phosphorous acid.** F. Loessner studied the action of **hypophosphorous acid.** R. E. Barnett noted that platinum pyrophosphate is formed when the metal is heated with **phosphorus pentoxide** in oxygen. According to C. Hüttner, a hot, conc. soln. of **phosphoric acid** attacks platinum in air, but not if air be excluded. C. W. Jurisch also noticed that molten phosphoric acid attacks platinum. B. Pelletier observed that glacial phosphoric acid attacks platinum in the presence of carbon. M. Schmöger found that platinum crucibles are not attacked at a red-heat by **magnesium pyrophosphate,** but if reducing conditions are present, W. C. Heraeus observed that the metal is disintegrated at 900°. The subject was discussed by G. E. F. Lundell and J. 1. Hoffman.

A. F. Gehlen [18] observed that when spongy platinum is heated with **arsenic,** the combination is attended by vivid incandescence; L. Wöhler prepared $PtAs_2$; and W. R. Hodgkinson and F. K. S. Lowndes found that a red-hot platinum wire is immediately fused when in contact with arsenic—*vide* **9.** 51, 10. A. F. Gehlen found that neither **arsenic trioxide** nor **arsenic acid** exerts any action on the metal—*vide* **9.** 51, 10. E. Mulder observed that platinum black transforms arsenic trioxide in aq. soln. into arsenic pentoxide, and C. Engler and L. Wöhler added that this occurs in the absence of air owing to the absorbed oxygen. J. H. Gladstone and A. Tribe observed the reduction of arsenious acid in aq. soln. to arsenic by hydrogenized platinum. H. E. Patten observed that platinum is blackened by **arsenic trichloride ;** and L. Kahlenberg and J. V. Steinle observed no reaction

with arsenic trichloride and platinum at ordinary temp. or at 100°. A. F. Gehlen, and F. Rössler observed that **antimony** reacts when it is heated with platinum very much as does arsenic, and the alloys were studied by V. A. Nemiloff and M. M. Voronoff, and T. J. Poppema and F. M. Jäger—*vide* **9.** 52, 9; and H. E. Patten found that the metal is not attacked by **antimony pentachloride.** A. F. Gehlen, C. T. Heycock and F. H. Neville, and F. Rössler also noted that **bismuth** readily unites with platinum when a mixture of the two elements is heated—*vide* **9.** 53, 7. For the action of **bismuth oxide,** *vide infra.* F. E. Brown and J. E. Snyder found that **vanadium oxytrichloride** has no action on platinum.

J. B. J. D. Boussingault,[19] and A. Colson found that at a red-heat platinum does not unite with **carbon.** N. W. Fischer observed that in the inner cone of the flame of a spirit-lamp, the surface of the metal is corroded. R. Chenevix and H. V. Collet-Descotils found that in a high temp. furnace, platinum forms a fusible carbide, and J. B. J. D. Boussingault suggested that the presence of silicon favours the breakdown of platinum under these conditions. A. B. Griffiths, and A. Rémont also noted that platinum is attacked by carbon at a red-heat—*vide* **5.** 39, 20. F. E. Carter observed no serious contamination when cast in graphite moulds, but the metal even below the m.p. readily takes up carbon, and on cooling, the carbon settles out between the crystal grains making the metal brittle and darker in colour. The diffusion of carbon in platinum was studied by G. Tammann and K. Schönert. F. Wöhler noted that the presence of platinum increases the combustibility of carbon. H. Wölbling studied the absorption of platinum by active carbon. M. W. Travers noted the absorption of carbon by spluttered platinum; and W. P. White, the absorption of impurities by platinum at a high temp. M. S. Belenky and co-workers, and S. Lewina and co-workers, studied activated carbon metallized with platinum.

The action of **carbon monoxide** on platinum has been discussed, **5.** 39, 27. W. Davies observed that combustion begins at 400°. A. Sieverts and E. Jurisch found that carbon monoxide at 1136° is insoluble in compact platinum; and E. Harbeck, and E. Harbeck and G. Lunge, thought that with platinum black a definite compound of carbon monoxide is formed, because the 60 vols. of carbon monoxide absorbed at ordinary temp. are suddenly liberated at 250°. B. W. Bradford studied the thermionic emission during the oxidation of carbon monoxide. H. S. Taylor and R. M. Burns showed that at 25°, 110°, and 218°, 1 vol. of spongy platinum absorbed, respectively, 1·20, 0·85, and 0·45 vol. of carbon monoxide, and at 25° and 110°, platinum black absorbed, respectively, 18·0 and 19·7 vols. of carbon monoxide. A. F. Benton said that at 25°, and 1 atm. press., platinum black absorbed 37·8 vols. of carbon monoxide. B. Delachanal observed that 3·19 to 4·05 c.c. of carbon monoxide were absorbed by about 150 grms. of commercial platinum. A. Osawa observed that the arrangement of the atoms in the space-lattice of platinum black is not affected by the absorption of carbon monoxide, but there is a linear expansion of 2·8 per cent. C. Paal showed that carbon monoxide is oxidized at ordinary temp. in the presence of a soln. of colloidal platinum. K. A. Hofmann and O. Schneider found that the catalytic activity of the platinum metals in the oxidation of carbon monoxide in the presence of a soln. of sodium chlorate, decreases in the order Os, Rh, Au, Pt, Ru, Pd, Ir, and Ag. F. P. Bowden and E. K. Rideal, A. Hocart, W. Davies, and A. E. Mitchell and A. L. Marshall discussed the subject. G. I. Finch and D. L. Hodge, A. S. Ginsberg and A. P. Ivanoff, G. M. Schwab, and C. R. Prichard and C. N. Hinshelwood studied the effect of the presence of other metals. D. Tommasi, F. H. Pollard, A. de Hemptinne, J. C. Stimson, G. I. Finch and J. C. Stimson, and L. Mond and co-workers observed the absorption of a little carbon monoxide. The subject was studied by I. Langmuir, A. J. F. de Silva, P. V. McKinney and E. F. Morfit, B. S. Srikantan, and W. G. Palmer. I. L. Bell found that carbon monoxide is not decomposed when it is heated with platinum; G. Orloff noted the pyrogenetic oxidation of carbon monoxide and hydrogen in contact with platinum. L. Wöhler

observed that in a mixture of hydrogen and carbon monoxide, the former gas is oxidized in the presence of platinum black more rapidly than the latter. The subject was studied by W. Davies. H. B. Dixon found that dry carbon monoxide is completely oxidized in the presence of dry oxygen and a glowing platinum wire. M. Traube noted that some hydrogen dioxide is formed when moist carbon monoxide is oxidized in the presence of platinum. J. J. Coquillion studied the action of platinum on a mixture of water vapour and carbon monoxide. E. von Meyer, and M. Faraday noted that carbon monoxide retards the activity of platinum on a mixture of hydrogen and oxygen. P. Sabatier and J. B. Senderens observed that platinum below 420° does not induce the hydrogenization of carbon monoxide to methane. The reaction was studied by E. F. Armstrong and T. P. Hilditch. G. O. Kemp observed that in the presence of platinum, carbon monoxide is oxidized by nitrous oxide forming nitrogen and carbon dioxide. A. Baikoff found that the platinum thermocouple, in a gas flame, disturbs the equilibrium of the gases. F. Fischer and co-workers compared the activity of the platinum metals in the hydrogenation of carbon monoxide to methane; and V. Voorhees and R. Adams, the platinum oxides with platinum black. A. Gutbier and W. Schieferdecker studied the action of hydrogen on carbon dioxide in the presence of platinum. According to P. Schützenberger, and W. Pullinger a mixture of carbon monoxide and chlorine forms platinum carbonyl chlorides with heated platinum. L. Mond and co-workers observed that a little **carbon dioxide** is absorbed by platinum. H. S. Taylor and R. M. Burns observed that at 25°, 110°, and 218°, 5 grms. of spongy platinum absorbed, respectively, 3·30, 2·60, and 2·10 c.c. of carbon dioxide, in all cases less than 0·05 vol. per vol. of platinum; with platinum black at 25° and 110°, 1·70 and 0·85 vols. of carbon dioxide were absorbed respectively. Observations were also made by A. F. Benton, J. C. Stimson, G. I. Finch and J. C. Stimson, and L. H. Reyerson and L. E. Swearingen; and B. Delachanal found that 0·51 to 0·70 c.c. of carbon dioxide was absorbed by about 150 grms. of commercial platinum. G. B. Taylor and co-workers gave approximately 25,000 cals. for the heat of adsorption. H. Dobretsberger studied the effect of absorbed carbon dioxide on the high-frequency resistance of platinum. A. Morren found that at a white-heat platinum decomposes carbon dioxide; and W. Muthmann and A. Schaidhauf, that platinum influences the dissociation of carbon dioxide in the high-tension arc. T. Bergman observed that carbonic acid does not attack platinum. B. S. Srikantan, and I. Langmuir studied the catalytic decomposition of carbon dioxide and water by platinum. According to P. Sabatier and J. B. Senderens, platinum below 420° does not induce the hydrogenization of carbon dioxide to methane. C. R. Prichard and C. N. Hinshelwood, B. S. Srikantan, M. Temkin and E. Mikhailova, and L. Duparc and co-workers studied the reduction of carbon dioxide in the presence of platinum as catalyst. J. H. Robertson found that dry **carbonyl chloride** is a useful reagent for the volatilization of the platinum metals; the optimum temp. is about 500°. B. S. Srikantan studied the reactions $H_2+CO_2=CO+H_2O$ in the presence of platinum. J. Milbauer and J. Doskar studied the catalytic action of platinum on the oxidation of **carbon disulphide** by sulphuric acid; and J. Milbauer, its action on the decomposition of **carbonyl sulphide.** J. B. Dumas found that **sulphocarbonates** in the presence of spongy platinum are immediately decomposed in air and water.

W. W. Randall found that **methane** does not diffuse through heated platinum. W. P. Yant and C. O. Hawk studied the effect of platinum in the oxidation of methane. According to H. S. Taylor and R. M. Burns, at 25°, 110°, and 218°, one gram of spongy platinum absorbs respectively, 3·45, 2·60, and 2·05 c.c. of **ethylene,** or less than 0·05 vol. of gas per vol. of platinum; and at 25°, and 110° with platinum black, respectively, 7·70 and 6·00 vols. of gas per vol. of metal are absorbed. M. Faraday noted that, like carbon monoxide, ethylene retards the activity of platinum in a mixture of hydrogen and oxygen. V. N. Morris and

L. H. Reyerson, and L. H. Reyerson and L. E. Swearingen studied the adsorption of methane and ethylene. P. Sabatier and J. B. Senderens observed no catalytic action of finely-divided platinum in the thermal decomposition of ethylene. K. S. Ablezova and S. Z. Roginsky, O. Beeck, M. Tauber, O. Schmidt, J. Eckell, R. Burstein and A. Frumkin, A. W. Gauger, G. B. Taylor and co-workers, G. Bredig and R. Allolio, B. Bruns and K. Ablezova, and K. Bennewitz and W. Neumann studied the hydrogenation of ethylene with a platinum catalyst; R. C. Cantelo, and M. Tauber, studied the decomposition of ethylene and ethane in the presence of platinum; I. E. Adaduroff, the dehydrogenation of *cyclo***paraffins**; and H. W. Underwood, S. Lenher, S. Lenher and I. R. McHaffie, J. Errera and V. Henri, N. P. Zelinsky and M. D. Turowa-Pollak, G. Lunge and J. Akunoff, W. D. Bancroft and A. B. George, and R. H. McKee and F. A. Strauss, platinum as a catalyst in general hydrogenations—*e.g.* H. von Euler and A. Oelander, with formic acid; P. de Wilde, C. Paal and A. Schwarz, C. Paal and C. Hohenegger, and W. Caro found that in the presence of hydrogen and colloidal soln. of platinum, ethylene is reduced to ethane; and **acetylene** to ethylene and ethane; G. Vavon, the hydrogenation of **limonene**; R. Fort and C. N. Hinshelwood, the oxidation of **benzene**, and W. G. Palmer studied the adsorption of benzene by platinum, J. W. Smith, by amalgamated platinum; R. C. Kirk and W. E. Bradt, the electro-oxidation of **toluene**; and N. D. Zelinsky and co-workers, the hydrogenation of benzene, and the dehydrogenation of **hexamethylene**. E. W. R. Steacie and R. Morton studied the thermal decomposition of **propaldehyde**; and H. A. Taylor, the decomposition of **acetone** in contact with platinum. J. J. Redwood, and J. H. Vogel noted that the acetylene flame increases the weight of a platinum crucible by carbonization. O. Angelucci found spongy platinum favours the formation of ammonium carbonate from acetylene and nitric oxide at 800°. E. Tiede and W. Jenisch examined the influence of platinum in the pyrogenic decomposition of acetylene. I. Horiuti and M. Polanyi observed an exchange of H^2 and H^1 in $H^2{}_2O$, C_2H_4 and in C_6H_6 at 80°, but not at room temp. The increase in weight which occurs when platinum crucibles are heated in **coal-gas** was observed by T. Wilm, F. Mylius and C. Hüttner, and A. Rémont; and observations on the subject were also made by S. Kern, P. Schützenberger and A. Colson, A. Colson, C. L. Berthollet, C. G. Memminger, T. Kariyone, J. B. J. D. Boussingault, V. Meyer, and A. B. Griffiths. E. B. Maxted and V. Stone studied hydrogenation of crotonic, oleic, and benzoic acids. According to T. Wilm, the action of platinum on coal-gas differs from that of palladium on the one hand, and of rhodium on the other. Only after a long time can any deposition of carbon be observed, which then takes place on the margin of the platinum, whilst the middle maintains its grey metallic appearance, nor does any alteration in vol. occur. In one case, when the action had gone on for an hour and a half, the weight of the metal had increased by 3·28 per cent., the formula PtC requiring 5·7 per cent. of carbon. On exposure to the air, the contents of the vessel underwent no change, but on passing a current of air over the heated mass, the carbon was completely burnt. Platinum, therefore, appears to produce a separation of carbon by contact action, as in the case of palladium, but, unlike the latter, the carbon is deposited in the pores of the metal without changing its volume, and not on the surrounding walls of the crucible, whilst rhodium forms a loose combination with the element. R. J. Wysor found the corrosion of platinum crucibles is less with a Méker burner than with a bunsen burner. O. L. Erdmann discussed the grey film formed when platinum is heated only in an oxidizing flame.

The catalytic hydrogenation, oxidation, and dehydrogenization of hydrocarbons, etc., was studied by F. Bellamy, M. Bodenstein, B. Bruns and K. Ablezova, W. Caro, J. J. Coquillion, J. J. Coquillion and J. Henrivaux, N. Demjanoff and M. Dojarenko, M. Faillebin, A. S. Ginsberg, E. Harbeck and G. Lunge, C. Harries and K. Gottlob, G. S. Hiers and R. Adams, E. W. Leitz and F. Seitz, V. B. Lewes, G. Lunge and J. Akunoff, R. F. Marchand, E. B. Maxted and C. H. Moon, C. H. Neilson, C. Paal and W. Hartmann,

F. C. Phillips, P. Sabatier and J. S. Senderens, O. Schmidt, A. Schwarz, H. Wieland, P. de Wilde, R. Willstätter and D. Hatt, and N. D. Zelinsky; A. A. Balandin, cyclohexane; aldehydes and ketones, A. Bringhenti, P. Sabatier and J. B. Senderens, A. Skita and W. A. Meyer, A. Trillat, and G. Vavon; alcohols, E. Bjelouss, A. Bringhenti, J. W. Döbereiner, S. Fokin, A. Glaessner, E. F. Gorup-Besanez, E. Grimaux, S. F. Hermbstädt, J. von Liebig, M. Martens, E. Orloff, Lord Rayleigh and W. Ramsay, P. Sabatier and J. B. Senderens, O. Schmidt, C. F. Schönbein, E. Sell, and A. Trillat; organic acids and salts, H. Behrens, C. F. Boehringer, J. Boëseken, R. F. Brunel, C. Dittrich, J. W. Döbereiner, E. Fischer, S. Fokin, O. Loew, O. Loew and K. Aso, N. A. E. Millon and J. Reiset, C. Paal and co-workers, F. Russ, P. Sabatier and co-workers, A. Schwarz, F. W. Schweigger-Seidel, O. Sulc, V. Vrabely, and N. D. Zelinsky and N. Glinka; sugars and starches, J. W. Döbereiner, C. H. Neilson, F. Plzak and B. Husek, B. Rayman and O. Sulc, M. Traube, and R. Vondracek; nitrogen compounds, H. Debus, H. G. Denham, K. Elbs, J. H. Gladstone, C. Paal and J. Gerum, J. D. Riedol, H. J. S. Sand, J. M. Thomson, and A. Trillat; and various other organic compounds, M. Ascoli and G. Izar, G. Bredig and F. Sommer, C. Foa and A. Aggazzotti, S. Fokin, E. Knoevenagel and A. Tomasczewsky, W. Knop, R. Lespieau and G. Vavon, L. Liebermann, O. Loew, R. Majima, C. H. Neilson, L. Pincussohn, E. Schaer, A. Skita, A. Skita and H. H. Franke, O. Stark, J. Tafel and K. Naumann, M. Traube, G. Vavon, C. O. Weber, R. Willstätter and co-workers, and E. Windisch.

B. Neumann and E. Altmann studied the catalytic effect of platinum in the action of hydrogen on **carbon disulphide.** W. R. Hodgkinson and F. K. S. Lowndes found that a red-hot platinum wire in the vapour of **carbon tetrachloride** breaks up the compound into chlorine, carbon, etc. P. Schützenberger found that when **cyanogen** is passed over heated platinum, platinum carbide and nitrogen are formed. H. B. Dixon observed that red-hot platinum favours the oxidation of cyanogen to carbon dioxide. H. Sinozaki and R. Hara studied the oxidation of **hydrocyanic acid.** Molten **potassium cyanide** was found by L. Gmelin to attack platinum crucibles forming a potassium platinous cyanide; and H. St. C. Deville and H. Debray observed that when potassium cyanide is heated with platinum black, at 500° to 600°, the main reaction is symbolized: $4KCy+2H_2O+Pt=K_2PtCy_4+2KOH+H_2$; and a boiling, conc. soln. of potassium cyanide attacks the metal, forming the same complex salt. H. Rössler observed no action with aq. soln. of potassium cyanide on platinum; and A. Brochet and J. Petit observed that in the cold the solubility of platinum is nil, but dissolution commences at about 100°. According to F. Glaser, the dissolution of platinum does not occur when mercury is being electrodeposited from potassium cyanide soln. containing sulphuric acid, potassium sulphate, hydrocyanic acid or ammonium cyanide when the temp. is low, say 15° to 20°, and the current is weak. The dissolution of platinum in soln. of potassium cyanide occurs at a higher temp., say 25° to 30°. Platinum dissolves in soln. of potassium cyanide in the absence of oxygen, and hydrogen is evolved. The solubility is very small in the cold, but is increased by a rise of temp., or by the presence of sodium or potassium amalgam. L. Wöhler observed that with platinum black the solubility is favoured by oxygen, or hydrogen dioxide. H. St. C. Deville and H. Debray found that mercury is not precipitated by platinum from a boiling aq. soln. of **mercuric cyanide,** but if a little potassium cyanide is present, mercury is deposited and it combines with the platinum. C. Marie observed that platinum is attacked by a 12 per cent. soln. of **potassium ferrocyanide** in a 2 per cent. soln. of sodium hydroxide. G. Just noted the catalytic oxidation of ferrocyanides in alkaline soln. by platinum. S. Cooke, J. H. Gladstone, and G. Just noted the reduction of **potassium ferricyanide** by hydrogenized platinum. C. Marie observed that an alkaline soln. of potassium ferricyanide slowly attacks platinum. E. Raub studied the action of onion, leek, and mustard juices.

A. Trillat studied various reactions catalyzed by a hot spiral of platinum; G. F. Hüttig and E. Weissberger studied the catalytic decomposition of **methyl alcohol** by platinum; and B. S. Srikantan, the efficiency of platinum as a catalyst. W. G. Palmer studied the adsorption of **ethyl alcohol** by platinum. E. Müller and K. Schwabe studied the oxidation of ethyl alcohol by a platinum catalyst, and L. B. Loeb, the heat of oxidation. A. Bringhenti found that alkaline soln. of the alcohols, or soln. of sodium methoxide, ethoxide, and n-propoxide are catalyti-

cally oxidized in the presence of platinum. Water retards the activity of the catalyst on the alkoxides. An e.m.f. is developed when electrodes of platinized and smooth platinum are dipped in an alcoholic soln. of sodium alkoxide. M. Tauber studied the voltaic potential of platinum during hydrogenations, and R. Köppen, the effect of the substance supporting the platinum on its catalytic action. M. S. Platonoff studied the adsorption of fumaric, maleic, itaconic, mesoconic, and citraconic acids. B. Bruns and co-workers studied the formation of acid oxides on the surface of platinized charcoal; E. B. Maxted and V. Stone, the poisoning of the catalyst. W. E. Grove and A. S. Loevenhaut said that the supposed hydrolysis of starch by platinum black is really due to the presence of platinum oxides in the platinum black. M. S. Platonoff and co-workers studied the adsorption of **organic acids** by platinum black; W. H. Carothers and R. Adams, and M. Faillebin, the hydrogenation of aldehydes and ketones; F. Sigmund, the hydrogenation of phenylacetaldehyde di-n-propylacetal, cinnamaldehyde diethylacetal, and benzaldehyde diethylacetal; H. P. van Beck, **formaldehyde**; V. Haas, G. Käb, C. N. Hinshelwood and B. Topley, H. C. Tingey and C. N. Hinshelwood, C. H. D. Clark and B. Topley, and E. Müller and co-workers, **formic acid**; and F. Berezovskaya and co-workers, **fumaric and maleic acids** in light. A. Skita noted the greater activity of colloidal platinum over spongy platinum in the hydrogenation of the nucleus of cyclic compounds—phenylene-2-acetic-2-propionic acid, benzylamine, β-phenylethylamine, iso-quinoline. J. W. Kern and co-workers studied the reduction of olefines; A. S. Ginsberg and A. P. Ivanoff, the hydrogenation of aliphatic compounds; J. S. Pierce and co-workers, the reduction of furylalkylcarbinols; H. Heckel and R. Adams, the reduction of aminophenols to cyclic amino-alcohols; N. D. Zelinsky and M. B. Turowa-Pollak, benzene; W. H. Carothers and R. Adams, the reduction of aldehydes—*e.g.* benzaldehyde; E. Waser, benzoic acid, nitroantipyrine, vanillylidehippuric acid, antipyrine, benzamido-cinnamic acid, and cinnamyl alcohol; R. Willstätter and F. Seitz, naphthalene; W. E. Kaufmann and R. Adams, furfuraldehyde; M. Faillebin, aldehydes and ketones; H. L. Lochte and co-workers, and K. A. Taipale, azines, ketazines, semicarbazones, and phenylhydrazones; G. Vavon, limonene; G. Vavon and A. Husson, cyclohexane, nitrobenzene, cinnamic acid, and acetophenone; R. Willstätter and D. Jaquet, indole, and the anhydrides of the o-dicarboxylic acids—*e.g.* phthalic anhydride and naphthalic anhydride-phthalic acid, naphthalic acid, and p-toluic acid; R. Willstätter and D. Hatt, benzene, naphthalene, durene, phenol, aniline, benzoic acid, pyrrole, *iso*-hæmopyrrole, *m*-chlorotoluene, and allyl bromide; K. Hess, α-1-methylpyrrylpropane-β-ol, 2-pyrrylpropane-$\beta\gamma$-diol, 2-acetylpyrrole, and 2-propionylpyrrole; C. Paal and W. Hartmann, and C. Paal and A. Schwarz, phenylpropiolic acid; J. Böeseken and co-workers, cinnamic, muconic, aconitic, itaconic, citraconic, mesaconic, cyclopropane-1 : 1-dicarboxylic, ethylenetricarboxylic, and vinylglycollic acids; F. Sigmund, the hydrogenation of aromatic aldehydes; E. W. R. Steacie and H. N. Campbell, the decomposition of ether; P. C. Allen and C. N. Hinshelwood, the decomposition of acetaldehyde; the decomposition of benzoyl peroxide and hydroperoxide, by F. I. Berezovskaya and O. Semikhatova; N. D. Zelinsky and A. A. Balandin, the dehydrogenations of decahydronaphthalene; G. Cusmano and E. Cattini noted the catalytic oxidation of buchu-camphor in the presence of platinum black; E. Müller and K. Schwabe, the oxidation of alcohol; E. W. R. Steacie and H. N. Campbell, the decomposition of ether; M. S. Platonoff and co-workers, the adsorption of organic acids; V. Grignard, the hydrogenation of tertiary methylheptenols; R. Willstätter and E. W. Leitz, aromatic compounds; H. Wieland, the dehydrogenation of dextrose, gluconic acid, lactic acid, phenol, *m*-cresol, guaiacol, pyrogallol, aniline, alcohol, and acetaldehyde, but not tyrosine and uric acid; R. Willstätter and E. W. Mayer, benzoic acid, erucyl alcohol, geraniol, phytol, and cholesterol; C. Paal and J. Gerum, fumaric, maleic, and cinnamic acids, methyl cinnamate, and nitrobenzene; according to O. Loew and K. Aso, platinum black converts maleic into

fumaric acid, and reduces nitrobenzoic acid, and trinitrophenol; R. Vondracek, L. Lindet, F. Plzak and B. Husek, and B. Rayman and O. Sulc, studied the hydrolysis of sucrose; C. H. Neilson, the hydrolysis of ethyl butyrate; E. Schaer, oxidations by benzoic peroxide, and quinone; H. A. Taylor and M. Schwartz, and E. W. R. Steacie and co-workers, the thermal decomposition of dimethyl ether, and diethyl ether; B. Bruns and M. Wanjan, the inversion of sugars; H. A. Taylor, the decomposition of acetone; K. Suzuki, geraniol; L. Michaelis and E. S. G. Barron, the reduction of cysteine; Y. Shibata and K. Yamasaki, the oxidation of pyrogallol; G. K. Hughes and co-workers, the reduction of the bromoalkylbarbituric acids; Y. Shibata and K. Yamasaki, the oxidation of pyrogallol; A. S. Richardson and A. O. Snoddy, the hydrogenation of cotton-seed oil; E. B. Maxted and C. H. Moon, the oxidation of crotonic acid; and F. Thoren, the catalase action. E. Salkowsky found that glacial **acetic acid** even when mixed with hydrogen dioxide does not attack platinum. W. G. Palmer studied the absorption of acetic acid by platinum. J. H. Mathews observed that a soln. of **trichloroacetic acid** in nitrobenzene does not attack platinum; and J. L. Sammis observed that a soln. of **copper oleate** in various solvents, and C. B. Gates, that **oleic acid** do not attack the metal. A. Carpené observed that the metal was not attacked on standing 192 hrs. in red **wine**; and W. Thomson and F. Lewis observed that platinum has an injurious effect on **indiarubber.** J. Ranedo studied the effect of platinum on the oxidation of organic matter by sulphuric acid.

H. Moissan[20] observed that **boron** contains platinum when it has been prepared in platinum vessels from a mixture of potassium and boric acid; and F. Wöhler and H. St. C. Deville observed that boron forms a boride when heated with platinum —*vide* **5.** 32, 4. A. Sieverts and K. Brüning studied the absorption of hydrogen by the platinum borides. O. Ruff and W. Menzel observed no reaction with **boron pentafluoride** below a dull red-heat. J. G. Rose observed that **borax** which has been fused in platinum vessels for 4 hrs. at a red-heat contained 0·3 mgrm. per 100 grms. H. V. Collet-Descotils observed that platinum is attacked by molten borax and carbon. L. Pissarjewsky studied the catalytic decomposition of **sodium perborate** by platinum. According to H. St. C. Deville,[21] H. N. Warren, F. P. Miles, and H. le Chatelier, **silicon** readily attacks platinum at an elevated temp.—*vide* **6.** 40, 14. F. C. Carter said that silicon forms a brittle alloy with platinum; and **silica** along with carbonaceous material or hydrogen has the same effect as indicated by L. I. Dana and P. D. Foote, J. B. J. D. Boussingault, and A. Guyard. I. Traube found that molten **potassium silicate** attacks platinum strongly; and W. P. White found silicates had in general no action below 900°. W. Jander said that molten silicates dissolve platinum not in the ionic form, but as metal; and at its m.p., platinum takes up iron from fused silicates in the presence of reducing gases. The attack of platinum crucibles by **iron silicates** was studied by T. Poleck, R. W. Mahon, W. Jander, and E. Isaak and G. Tammann. C. G. Memminger found that topaz fused in a platinum crucible under reducing conditions formed brittle platinum silicide. W. R. Hodgkinson and F. K. S. Lowndes observed that **silicon tetrafluoride** is decomposed by a red-hot platinum wire, forming crystals of silicon and platinum fluoride. K. Fuwa studied the coloration of **glass** by platinum. The catalysis of the oxidation of **titanous sulphate** by platinum black was studied by B. Diethelm, B. Diethelm and F. Förster, and H. G. Denham. H. Rose, and W. B. Giles noted that platinum crucibles are attacked by soln. of **titanic acid** in the presence of nitric or sulphuric acid.

The action of platinum on the **metals** is discussed below. The favourable action of platinum on the dissolution of metals in acids was discussed by L. H. Zenneck,[22] J. T. Conroy, and W. Ostwald. M. Philippson observed that when a platinum plate is introduced into colloidal **copper,** prepared by cathodic disintegration, copper is gradually precipitated. The precipitation is independent of the electrolytic soln. press. of the precipitating metals, and these metals, under the influence of the discharge of the colloidal particles during precipitation, are able in their turn

to assume the colloidal state. A. Trillat found that a trace of platinum favours the catalytic activity of copper. R. Engel noted the favourable action of platinum on the dissolution of copper in hydrochloric acid; and W. Nernst, on the dissolution of copper in a soln. of potassium cyanide. A platinum plate is without action on the hydrosol of **silver.** F. Vles and M. Get studied the effect of platinum on silver sols. F. C. Carter observed that platinum absorbs **calcium** when heated electrically in lime; M. Ballo, a trace of platinum favours the reducing action of **magnesium;** N. A. E. Millon, the dissolution of **zinc** in acids; L. Schönn, the dissolution of **cadmium** in nitric acid; and C. Barreswil, and N. A. E. Millon, that the presence of traces of platinum favours the evaporation of **mercury;** but F. C. Carter observed no tendency to amalgamation below 200°. M. Volmer and A. Weber studied the wetting of platinum by mercury; Y. Okayama, and A. I. Leipunsky, the oxidation of mercury by oxygen in the presence of a heated platinum filament. W. R. E. Hodgkinson and F. K. S. Lowndes observed no attack by mercury vapour on the red-hot wire; but T. Ihmori found that an adsorption of mercury vapour by platinum black occurs such that at 17°, a specimen of platinum black, 0·3 grm., increased in weight 0·0021 grm. in 5 hrs. Platinum foil showed no increase in weight. O. Loew found that with **hydrogen amalgam,** in water, heat is developed; and L. Cailletet, that with **ammonium amalgam,** or **sodium amalgam,** under water, platinum is amalgamated. E. B. Maxted noted the adsorption of **lead** or mercury which acts as a catalytic poison on platinum. L. Schönn noted that platinum favours the dissolution of **tin** in nitric acid; N. A. E. Millon, the dissolution of **iron** in acids; and L. Varenne, the depassivation of iron in conc. nitric acid. W. G. Imhoff studied the deleterious action of zinc on platinum. J. L. Gay Lussac and L. J. Thénard found that platinum is oxidized when heated with **potassium peroxide;** and W. L. Dudley, T. Poleck, L. Quennessen, and E. Leidié and L. Quennessen found that the metal is also attacked when heated with **sodium dioxide.** W. Dittmar, and L. Troost said that platinum is not attacked by **lithium oxide** in the absence of air at a white-heat; but R. Rieke and K. Endell observed that the metal is attacked in the preparation of molten lithium silicates in platinum crucibles. G. Brügelmann observed that the sp. gr. and crystal form of **barium oxide** made in platinum and in clay crucibles are different. According to P. Nicolardot and C. Chatelot, at 825°, barium oxide is much less corrosive than the alkali hydroxides. O. Sackur found that the metal is perceptibly attacked by barium oxide and **strontium oxide** at an elevated temp., and H. Rose noted that it is attacked likewise by **manganese dioxide;** and J. J. Berzelius, and G. Bischof, by molten **potassium hydroxide.** W. Dittmar observed that there is no attack by alkali hydroxides at a red-heat, when air is excluded, but if air has access, peroxides are formed and the metal is attacked. F. C. Carter, and M. le Blanc and L. Bergmann observed no attack by **sodium hydroxide** at 400°, but the metal is corroded at temp. exceeding 700°. T. Gross observed that in the electrolysis of fused potassium hydroxide, or of potassium carbonate mixed with a little nitrate, in a platinum crucible, at a yellow heat, with an alternating current of 50 cycles per second, 120 volts, and 35 amps., the metal is attacked, and needles resembling graphite are formed on and in the fused mass. J. J. Berzelius found that platinum is attacked by molten **lithium hydroxide,** and the subject was studied by W. Dittmar, L. Troost, L. N. Vauquelin, P. Nicolardot and C. Chatelot, H. A. von Vogel, and L. Kralovanszky. According to W. Skey, platinum is so affected by soln. of the fixed alkalies that it can no longer be amalgamated until the metal has been treated with acids. It was supposed that a film of oxide is formed on the metal. C. Marie observed that the metal is oxidized by an aq. soln. of potassium permanganate and sodium hydroxide. According to P. Nicolardot and C. Chatelot, platinum crucibles undergo marked corrosion when sodium hydroxide or potassium hydroxide is fused in them, and the crucibles are subsequently washed, first with water and then with dilute acid. New crucibles resist better than old crucibles, and the presence of iridium rather

diminishes the resistance to corrosion. Potassium hydroxide is decidedly more corrosive than sodium hydroxide. Observations were also made by L. Quennessen, and E. Leidié and L. Quennessen. L. L. de Koninck found that platinum is attacked by molten **alkali carbonates,** and this the more if manganese is present owing to the formation of alkali manganates; R. W. Mahon noticed that the action is also favoured by the presence of iron compounds. T. Gross observed an attack during the electrolysis of the fused carbonate—*vide supra.* J. J. Berzelius, L. Troost, and W. Dittmar also showed that **lithium carbonate** attacks platinum in air, presumably owing to the formation of lithium dioxide since, W. Dittmar showed that in nitrogen, the metal is not attacked. C. Kellner found that alkalies are adsorbed by platinum black; and W. Skey, that contact with alkalies or alkali carbonates affects platinum so that it does not amalgamate with mercury. E. J. Kohlmeyer and J. W. Westermann found that platinum is not attacked by **lead oxide** (also bismuth oxide) in a neutral atm. at temp. up to 1200°, but at 1300°, the slow dissociation of the oxide occurs, and platinum gradually absorbs the metal, forming fusible drops; at 1400°, rapid perforation of the platinum occurs. The **magnesium aluminite,** called Marquardt's body, attacks platinum at 1600°, and the crucible fails at 1700° owing to the absorption of magnesium, and aluminium by the platinum. Platinum wire roughens in contact with **magnesia** or with **alumina** at 1600°; and fails at about 1700°. E. Tiede and R. Piwonka studied the alumina.platinum phosphors.

W. Skey[23] observed that contact of platinum with chlorides prevents the metal amalgamating with mercury. According to G. Méker, finely-divided platinum is not attacked by fused **ammonium sulphate,** nor appreciably by **alkali bromides** between 250° and 350°; but a mixture of ammonium sulphate with **ammonium bromide** or **potassium bromide** forms red ammonium bromoplatinite; **ammonium chloride** in place of the bromide, also attacks platinum; and with **ammonium** or **potassium iodide,** iodine is liberated. A. Frumkin and A. Obrutscheva studied the hydrolytic adsorption of **sodium sulphate.** A mixture of **potassium sulphate** and **potassium bromide** also attacks platinum; and similarly with a mixture of potassium sulphate and **potassium chloride.** A. Frumkin and A. Donde found that platinized charcoal, activated in air, adsorbs acid from potassium chloride soln., and liberates alkali, whereas the opposite effect occurs in an atm. of hydrogen. The addition of thiocarbamide to the potassium chloride soln. poisons the platinum, and the charcoal then absorbs only acid independently of the atmosphere. Spongy platinum adsorbs alkali from a soln. of sodium sulphate; but spongy platinum which absorbs acid and liberates alkali in the presence of oxygen could not be prepared. J. Persoz, F. C. Carter, and W. F. Hillebrand found that molten **potassium hydrosulphate** attacks platinum. H. Weisz, and R. Schwarz and H. Stock, observed that platinum can serve as nuclei for the solarization of **silver bromide** films. E. Kraus observed that platinum is attacked by molten **calcium chloride** owing to the formation of some calcium oxide; and the reaction was studied by A. Petzholdt. E. Schaer noted that the presence of colloidal platinum favoured the oxidation of some organic substances by **cupric salts,** and also by **silver nitrate.** D. Tommasi studied the reduction of **silver chloride** by platinum. The effect of platinum on the photochemical reaction with **silver bromide**: $3AgBr \rightleftharpoons Ag_2Br + AgBr_2$ was studied by B. L. Vanzetti, W. J. Russell, and E. Cohen. V. Kohlschütter noted the reduction of soln. of **silver oxide** by hydrogen in the presence of a platinum catalyst. C. St. Pierre observed that a soln. of **auric chloride** is partly reduced by platinum. T. L. Phipson and D. Tommasi found that auric chloride is reduced by hydrogen in the presence of platinum. W. P. Jorissen and W. E. Ringer found that traces of platinum favour the phosphorescence of **zinc sulphide.** K. A. Hofmann and V. Wölfl observed that platinum separates **radium-F** from hydrochloric acid soln. of bismuth-polonium, and soln. of radium-lead chloride containing radium-D, and radium-F. R. Abegg and J. F. Spencer studied the oxidation of **thallous nitrate** with platinum anodes. E. A. Baur and A. Glässner

found that soln. of **ceric salts** are reduced by platinized platinum with the evolution of oxygen. W. R. Hodgkinson and F. K. S. Lowndes found that a red-hot platinum wire in the vapour of **mercuric chloride** furnishes some platinous chloride. H. Ley said that when a soln. of mercuric chloride is shaken with platinum, there is probably some reduction. R. Peters observed that when a soln. of sodium chloride is allowed to stand over mercury and a platinum wire is present, some mercuric chloride and sodium hydroxide are formed, and W. Skey observed a similar result with hydrochloric acid. E. Schaer noted that the presence of colloidal platinum favoured the oxidation of some organic substances by mercuric chloride. According to E. Alexander, platinum does not reduce a soln. of mercuric chloride in ethyl acetate. S. Cooke noted that mercuric salts are rapidly reduced by hydrogenized platinum. J. J. Berzelius noted the attack of platinum crucibles by **vanadium salts.** L. Pissarjewsky noted the catalytic reduction by platinum of the **vanadium salt** $K_8V_5O_{26}$ to KVO_4. J. C. G. de Marignac noted that platinum is attacked by fused **potassium columbium fluoride.** F. W. Tschirch observed that **osmium octofluoride** tarnishes platinum. E. Schaer noted that the presence of colloidal platinum favoured the oxidation of some organic substances by **chromic acid.** C. Marie found that platinum is oxidized by a normal soln. of **potassium dichromate** in N-H_2SO_4. C. Marie observed that an acidic soln. of potassium dichromate slowly attacks platinum. S. Cooke found that acidic soln. of potassium dichromate are rapidly reduced by hydrogen in the presence of platinum. C. F. Schönbein noted that soln. of **potassium chromate** in the presence of platinum black colour blue a soln. of starch and potassium iodide. M. Soller, and E. Müller and M. Soller found that with a smooth platinum anode, a soln. of **chrome alum** in N-H_2SO_4 is not appreciably oxidized to chromic acid, and with a platinized platinum anode, the oxidation proceeds about one-third as far as it does with an anode of lead dioxide. A. F. Joseph and W. N. Rae noted a marked attack by chromium phosphate at 1200°. The decomposition of soln. of **chromous salts,** $2Cr^{\cdot\cdot}+2H^{\cdot}=2Cr^{\cdot\cdot\cdot}+H_2$, was studied by T. Döring, K. Jablczynsky, and R. Peters. C. Fromme studied the electrochemical behaviour of **chromic acid** towards platinum—*vide* Bunsen's cell. A. Chilesotti studied the favourable action of platinum cathodes in the electrolytic reduction of **molybdates.** C. Paal and H. Büttner found ammonium molybdate is reduced by colloidal platinum. O. Ruff and co-workers observed that platinum resists the action of **tungsten hexafluoride,** but not of **uranium hexafluoride.**

C. Marie observed that platinum is oxidized by **potassium permanganate** in a 2 per cent. soln. of sodium hydroxide, or in sulphuric acid ; A. H. Allen, however, observed no attack with sulphuric acid containing potassium permanganate. W. Foster found that finely-divided platinum favours the reduction of potassium permanganate ; $2KMnO_4+H_2O=2KOH+Mn_2O_7$; and $Mn_2O_7+4H_2O=2Mn(OH)_4+3O$. C. Marie observed that acidic or alkaline soln. of potassium permanganate slowly attack platinum. E. Schaer noted that the presence of colloidal platinum favoured the oxidation of some organic substances by permanganates. R. Peters found **manganese trichloride** is very unstable in the presence of platinized platinum. W. Foster said that dil. neutral soln. of **potassium permanganate** are reduced by finely-divided platinum. R. B. Sosman and J. C. Hostetter, and J. W. Greig and co-workers found that at 1600°, in air, platinum reduces both **ferric oxide** and **ferrosic oxide,** oxygen is evolved, and a solid soln. of iron in platinum is formed ; and the reaction occurs at 1200° if the oxygen pressure is small. Hence platinum crucibles sometimes increase in weight if used to heat iron oxides at a high temp. J. Napier did not find platinum to be attacked by soln. of **ferric salts.** According to A. Béchamp and C. St. Pierre, J. Personne, H. Schild, A. L. Beebe, and D. Tommasi, **ferric chloride** is reduced to ferrous chloride by platinum ; and the subject was discussed by C. St. Pierre. C. Marie observed no attack by ferric chloride. E. Schaer noted that the presence of colloidal platinum favoured the oxidation of some organic substances by ferric salts. J. Eggert

studied the reduction of ferric salts by colloidal soln. of platinum. S. Cooke noted the reduction of ferric salts by hydrogenized platinum. E. Müller and G. Wegelin found that the presence of platinum favoured the reduction of ferric chloride by zinc; and R. Peters, W. Manchot and J. Herzog, and E. Oberer, the reduction of **cobaltic salts.** C. St. Pierre noted that **palladic chloride** is partially reduced by platinum, and E. Bose studied the equilibrium between platinum and **platinic chloride.** E. W. Hilgard found that spongy platinum favours the decomposition of **potassium chloroplatinate.** J. A. Buchner studied the action of **ammonium nitrate** on platinum. C. Claus, J. Lang, O. Köttig, and S. Tennant noted that fused **potassium nitrate** attacks platinum. The metal is also attacked by molten **barium and strontium nitrates.** H. St. C. Deville and H. Debray noted that when platinum is treated with **iron disulphide** in fused borax, platinum sulphide is formed.

According to A. Frumkin and A. Obrutscheva, if a hydrogen electrode is immersed in a soln. of a neutral salt, *e.g.* sodium sulphate, in which the osmotic press. of the hydrogen ions is less than the electrolytic soln. tension of the electrode, a small amount of hydrogen ions will pass into soln. and the resulting negative charge on the surface of the electrode will attract sodium ions from the soln., which will therefore become acid. A. Frumkin and A. Donde observed that purified spongy platinum, well-washed with purified water in an atm. of hydrogen, adsorbs alkali from a soln. of sodium sulphate; the alkali is not completely removed by washing with a considerable quantity of water, so that the amount of acid liberated is always in excess of that of the alkali. It has not been found possible to prepare spongy platinum in presence of oxygen which adsorbs acid and liberates alkali. Charcoal treated with platinum and activated in air adsorbs acid from potassium chloride soln. and liberates alkali, whereas the opposite effect is observed in an atm. of hydrogen. Addition of thiocarbamide to the potassium chloride soln. poisons the platinum, and the charcoal then adsorbs only acid independently of the gaseous atm. I. M. Kolthoff and T. Kameda also observed that platinized-platinum, in an atm. of hydrogen, adsorbs the cation from a neutral salt soln., and an eq. amount of free acid is formed in the soln. Zinc sulphate soln., in an atm. of hydrogen, increased in acidity to an extent eq. to the amount of zinc adsorbed by the platinum. Ammonium chloride likewise became slightly acid, but in oxygen such soln. became very distinctly acid, and the acidity increased the longer the oxygen was passed. This is attributed to the formation of hexa-aquoplatinic acid, which reacts with the ammonium ions present: $H_2Pt(OH)_6 + 2NH_4 \rightarrow (NH_4)_2Pt(OH)_6 + 2H$. Similar results were obtained with trimethylammonium and potassium chlorides. No acid adsorption from hydrochloric acid occurs in a hydrogen atm., but in an oxygen atm. there is eq. adsorption of hydrogen and chlorine ions. Sodium hydroxide is strongly adsorbed in a hydrogen atm.; maximum adsorption occurs at a concentration of $0{\cdot}0007N$. This adsorption is increased by addition of sodium chloride, and in presence of large amounts of the latter the maximum disappears. In the presence of oxygen the hexa-aquoplatinic acid formed neutralises some of the alkali, and only apparent adsorption of the latter, therefore, takes place. F. Tödt observed that the hydrolytic adsorption in phosphate buffer soln. containing potassium chloride, at a platinized-platinum surface, gives rise to acid in amount sufficient to account for the hydrogen effect observed by L. Wolff. H. Gall and W. Manchot studied the reducing action of hydrogen and platinum on various inorganic salts.

Reactions of platinum of analytical interest.—A soln. of hydrochloroplatinic acid gives no precipitate with hydrochloric acid, but the soln. gives yellow precipitates of the sparingly soluble chloroplatinates when treated with conc. soln. of **potassium or ammonium chloride.** When the soln. of hydrochloroplatinic acid is treated with **hydrogen sulphide** in the cold, platinum disulphide is slowly precipitated, the precipitation is faster with a warm soln. N. W. Fischer [24] observed that the limit of the reaction occurs with a soln. containing one part of platinum in 30,000 parts of liquid. According to R. Gaze, the precipitation is incomplete—

perhaps a colloidal soln. is formed—but if some mercuric chloride is present, the platinum disulphide is formed rapidly and completely along with the mercuric sulphide. U. Antony and A. Lucchesi observed that the precipitation is quantitative with conc. soln. at 90°, but not at 15° to 18°; with dil. soln., colloidal sulphide is formed. H. Reinsch observed no precipitation in soln. of one part of platinic chloride in 100 parts of water and 25 parts of hydrochloric acid; and N. W. Fischer added that the precipitate is soluble in hydrochloric acid. Actually the precipitated sulphide is insoluble in mineral acids, but readily soluble in aqua regia; it is slowly dissolved by alkali sulphides, but is more readily soluble in alkali polysulphides from which soln. it is precipitated by acids. A soln. of ammonium sulphide precipitates platinum sulphide; if **ammonium polysulphide** is employed the precipitation is slow in the cold, but faster with warm soln. Complete precipitation is attained with difficulty.

The soln. of hydrochloroplatinic acid is reduced by **stannous chloride** to hydrochloroplatinous acid, not to the metal; if the soln. is acidified with hydrochloric acid, and only a small proportion of platinum is present, the liquid becomes yellow, and, according to L. Wöhler and A. Spengel, there is formed a colloid analogous to purple of Cassius. N. W. Fischer said that the limit to the coloration is 1 part of platinum in 100,000 parts of liquid; and J. L. Lassaigne observed that 1 part in 10,000 parts of liquid gives a reddish-yellow liquid and a precipitate; with 20,000 parts of liquid, a paler reddish-yellow liquid; with 40,000 parts of liquid, an orange-yellow colour; with 80,000 parts of liquid, a yellowish-colour; but with 160,000 parts of liquid, a pale yellow; and with 640,000 parts of liquid, a very pale yellow colour. L. Wöhler and A. Spengel said that the sensitiveness of the test is 10^{-7} grm. of platinum in a c.c. of liquid; and R. Ruer, 0·01 mgrm. of platinum in 10 c.c. of liquid. A deep, reddish-yellow precipitate is produced by **mercurous nitrate.** R. Böttger found that a distinct yellow colour is produced by mercurous nitrate when 1 part of platinum is present in 100,000 parts of liquid. G. Forchhammer found the sensitiveness in the presence of nitric acid is 1 in 10,000. Unlike the corresponding reaction with gold, **ferrous salts** do not precipitate platinum from acidic soln. of hydrochloroplatinic acid; but in a soln. which has been neutralized with sodium carbonate, platinum is precipitated along with ferric hydroxide. Unlike gold also, **oxalic acid** does not precipitate the metal from soln. of hydrochloroplatinic acid. When treated with **alkali iodides,** hydrochloroplatinic acid is reduced to hydrochloroplatinous acid, with the separation of iodine, and A. Walcker, and F. Field arranged the conditions to detect 1 grm. of platinum in over 1,000,000 c.c. of soln. J. L. Lassaigne said that with 1 part of platinum in 10,000 parts of liquid, an orange-yellow colour passing to red is formed; with 20,000 parts of liquid, a yellow colour is produced which soon becomes red; with 40,000 parts of liquid, the colour is first yellowish and then rose coloured; with 160,000 parts of liquid, a rose colour is produced in a few minutes; and with 320,000 parts of liquid, a scarcely perceptible rose colour appears after some time. F. Emich and J. Donau said the sensitiveness is such as to detect 0·000005 grm. of platinum. G. G. Aquilina recommended **iodic acid** as a test for detecting platinum. O. Brunck found that **sodium hyposulphite** reduces platinic to platinous chloride with the precipitation of sulphur. R. Doht precipitated platinum by boiling the soln. with **hypophosphorous acid.** Unlike gold soln., metallic platinum is not precipitated from hydrochloroplatinic acid by **sulphurous acid, acetylene, hydroxylamine,** and **hydrogen dioxide** in alkaline soln.; and metallic platinum is precipitated from the hot soln. by **formic acid,** by **formaldehyde,** by **glycerol** and sodium hydroxide, by **hydrazine,** by **magnesium,** and by **zinc.** W. N. Ivanoff observed that soln. of platinum salts give a precipitate with **thiocyanate.** When platinum salts are boiled with **pyrocatechol** or **pyrogallol,** a blood-red soln. is produced which changes to dark brownish-red; and when a platinum salt soln. is made alkaline with ammonia, the same coloration is produced with **resorcinol** (S. C. Ogburn). W. Singleton recommended as tests for platinum, ammoniacal

resorcinol soln., reduction with stannous chloride, microscopical test with hexamethylenetetramine or potassium chloride, addition of sodium thiocyanate and ammonium nitrate. According to E. Sonstadt, when **mercury** of a high degree of purity is agitated with a soln. of 1 part of platinochloride in 3,000,000 parts of water, the precipitation of platinum can be recognized. G. Malatesta and E. di Nola found that with very dil. soln. of hydrochloroplatinic acid, **benzidine** in acetic acid soln. gives a flocculent bluish precipitate. The sensitiveness is equal to 0·0000125 part of platinum. V. G. Chlopin said that platinous salts give no precipitate, and conc. soln. of platinic salts, a rose-red precipitate. M. Wunder and V. Thuringer found that the precipitation with **dimethylglyoxime** is not quantitative. R. Meldrum detected 1 part of platinum in 5000 parts of liquid by precipitation with **potassium ferrocyanide.**

The physiological action of platinum salts.—The toxic and corrosive action of platinum salts introduced in the stomach of animals was observed by C. G. Gmelin.[25] According to F. Höfer, a dose of 1·25 grms. of platinum chloride or 1·87 grms. of sodium chloroplatinate, has a marked poisonous action. Conc. soln. of platinic chloride produce irritation of the skin, and erythema ; the mucous membrane is irritated, and the brain is affected. Sodium chloroplatinate has a milder action. The therapeutic action has some analogies with those of mercury, iodine, gold, and arsenic, but platinum salts act less strongly than auric or mercuric chlorides. Platinum salts were once used as remedies for syphilis, and rheumatic affections. J. A. Blake said that the lethal dose for injections is 0·02 mgrm. per kgrm., and that the relative toxic actions of gold, platinum, and lithium are as $1 \cdot \frac{1}{10} : \frac{1}{27}$. R. S. Hardman and C. H. Wright reported that a child accidentally swallowed 8 grains of potassium chloroplatinite. This was attended by vomiting and diarrhœa with the usual symptoms of gastro-enteritis ; the child collapsed, and in spite of treatment, died from cardiac failure in five hours. At the autopsy, the mucous membrane of the stomach was found to be pale except for a patch of brownish-yellow staining on the posterior wall ; the spleen was enlarged and the kidneys, highly congested, displayed punctiform hæmorrhages ; a chronic intussusception was found which possibly had something to do with the fatal termination. Platinum was found in the stomach and intestines. J. A. Blake studied the relation between the valency and the biological action of platinum salts ; and F. Hofmeister found that increasing the number of NH_3-groups in the platinum ammines favours the development of the toxicity, but differences in constitution and valency had no appreciable effect. J. Dunin-Borkowsky and Z. Szymanowsky observed no connection between the agglutinating and hæmolyzing power of salts of the heavy metals and the valency or chemical relationships of the metals.

C. Foa and A. Aggazzotti observed that intravenous injections of colloidal platinum had no perceptible effect on dogs. A. Robin and G. Bardet found that the colloid increased the separation of urea, uric acid and indoxyl, and raised the respiratory quotient. M. Ascoli and G. Izar showed that when administered to man hypodermically and intravenously, there is an increase in the output of nitrogenous compounds. W. Chonstein studied the effect of subcutaneous or intravenous injection of sodium chloroplatinate on the elimination of nitrogen compounds. According to J. Jütt, oxyhæmoglobin readily forms compounds with salts and double salts of the heavy metals ; the compounds thus obtained are very sparingly soluble in blood, especially in the presence of sodium chloride. The metallic compounds are obtained by the replacement of five hydrogen atoms in oxyhæmoglobin by five atoms of a metal, the valency of the metal appearing to be without influence. The main action of heavy metals as poisons is that the formation of the metallic compounds with the oxyhæmoglobin renders the blood incapable of acting as an oxygen carrier. The physiological action of platinic chloride was studied by A. W. Pell. J. Feigl and A. Rollet found that the colloid has a specific action in promoting the gastric secretion of a dog, which is not possessed by metals when administered in the form of ordinary ionizable salts. A. Robin and G. Bardet

observed that in some infectious maladies, the colloid promoted oxidation of the tissues, and the cure of the disease. C. Levaditi and co-workers found the double thiosulphate of platinum and sodium to be less active than the corresponding salt of gold in its trypanocidal action on rabbits.

Compact platinum was found by H. Thiele and K. Wolf to have no baneful action on bacteria. E. Behring, L. Bitter, E. Rosenthal and W. Bamberger, and the Farbwerke vorm. Meister, Lucius und Brüning studied the value of platinum salts as antiseptics; A. Calmette, A. Pedler, and T. L. Brunton and J. Fayrer, as antidotes for snake poisoning. H. Micheels and P. de Heen, the favourable action on the germination of wheat; A. Chassevant and C. Richet, the inhibiting action on the lactic fermentation of whey; A. Devaux, the non-fixation of platinum by the cell walls of plant stems from which the calcium and magnesium salts have been abstracted by acids; and T. Thunberg, the null-effect of hydrochloroplatinic acid on the absorption of oxygen by lecithin.

Some uses of platinum.—C. Ridolfi [26] tried plating copper and brass with platinum leaf to make stills and evaporating pans, but not successfully. Platinum plating gives a non-tarnishable coating for silver and base metals. Platinum generally alloyed with 10 per cent. of iridium has been employed in making standard international measures of length, and weight; the metal is employed in the production of mirrors, and cross-wires for optical instruments; and in the construction of pyrometers—*e.g.* thermo-couple, contact breakers and resistance pyrometers, as well as optical pyrometers. The metal is used in the construction of chemical apparatus—*e.g.* crucibles, gooch filters, electrodes, etc. K. Falck described the use of platinum in dental work as alloys and pins for artificial teeth, foil for crowns, and supports for dentures; in electro-analytical work, a catalyst in numerous chemical reactions—the oxidation of ammonia, and of sulphur dioxide—and in the construction of automatic gas-lighters; in the electrical industries for glass-to-metal joints, and for various contacts particularly if arcing is liable to occur. Platinum or platinum-iridium points are used for hypodermic syringes, and for cautery points. Platinum or a gold-platinum alloy is used in the artificial silk industry for spinnerets; and for spraying jets in the manufacture of sulphuric acid. Platinum and its alloys are used as a non-magnetic substitute for steel in some chronometers and watches. It has been tried in the construction of incandescent lamps, as a resistance material in the construction of electrically heated muffles, as platinum points in magnetos for aeroplane motors, etc. Investigations are being made of platinum-iridium flutes which are said to have a greater purity of tone than flutes made of other materials. The salts of platinum are also employed as reagents—*e.g.* in the determination of potassium, rubidium, and cæsium—and in photographic work—*e.g.* in platinum printing, and toning.

According to B. N. Menschutkin, in 1828, the Russian Government had accumulated large stores of platinum from the Uralian districts, and the metal was minted as coins of 3, 6, and 12 roubles. This was continued until 1845, when the minting was stopped and the coins withdrawn from circulation, the reason being that the Russian Government was unable to fix and maintain the price of the metal, so that large quantities of coins passed to other countries. Some platinum medals have also been struck. Platinum is also employed in jewellery.

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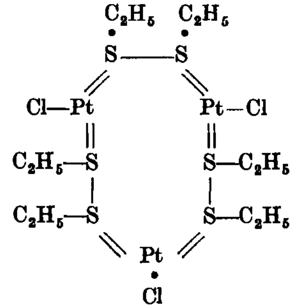
§ 15. The Atomic Weight and Valency of Platinum

Platinum forms the two chlorides—$PtCl_2$ and $PtCl_4$—where the metal is respectively *bivalent* and *quadrivalent*. This is confirmed by the two oxides, PtO, and PtO_2. Platinum is univalent in the platinum monochloride studied by S. Streicher,[1] L. Wöhler and S. Streicher, and W. Manchot and G. Lehmann obtained evidence of the formation of univalent platinum—*vide infra*, platinum suboxide. Platinum is *tervalent* (i) in an ill-defined brown oxide, and hydrated oxide, (ii) in platinum trichloride studied by F. Martin, L. Wöhler and F. Martin, P. C. Ray and N. N. Ghosh, and L. Pigeon; (iii) in M. Blondel's yellow acid, $HPt(SO_4)_2.6H_2O$, and in the yellow potassium salt, $KPt(SO_4)_2.H_2O$; (iv) in S. M. Jörgensen's reddish-brown α-$Pt(NH_3)$ en Br_3, and the analogous red α-$Pt(NH_3)$ py Cl_3; (v) in L. A. Tschugaeff and I. I. Tscherniaeff's black β-$Pt(NH_3)_2(OH)Cl_2$, and the red $PtenCl_3$, and in the red crystals obtained by H. D. K. Drew and co-workers by mixing α-[$Pt(NH_3)$ en Cl_2] and α-[$Pt(NH_3)$ en Cl_4]; and (vi) in the palladium salts and in the black $Pt(NH_3)_2Cl_3$ prepared by H. D. K. Drew and co-workers. E. G. Cox and co-workers discussed the planar structure of complex salts of bivalent platinum. J. F. Heyes said that the metal at high temp. behaves as a bivalent element, and at ordinary temp. as a quadrivalent element. W. Biltz discussed the effect of temp. on the valency of platinum towards oxygen. F. Kohlrausch deduced from his electrolytic observations that the metal behaves as if its valency were between 2 and 3, and L. Holborn and L. Austin obtained a similar conclusion from observations on the cathodic spluttering of platinum. The platinum chlorides, nitrites, etc., exhibit a strong tendency to form complex molecules so that the platinum in potassium nitritoplatinite, $K_2Pt(NO_2)_4$, and in potassium chloroplatinite, K_2PtCl_4, behaves as if it were sexivalent; and in potassium chloroplatinate, K_2PtCl_6, as if it were octovalent. The constitution of these salts, and of the ammines has been discussed by I. I. Tscherniaeff, A. A. Frinberg, C. W. Blomstrand, F. P. J. Dwyer and D. P. Mellor, P. T. Cleve, S. M. Jörgensen, A. Werner, etc., in connection with the ammines—**49**. 19—and the cobaltammines—**67**. 17, 1835. The primary valency of platinum in the chloroplatinates is four. The subject was discussed by T. M. Lowry. H. Töpsöe considers the complex chlorides of the type: $2RCl.PtCl_4$ are isomorphous with the analogous complex fluorides of tin, titanium, zirconium, and silicon, and the analogous chlorostannates; and I. Bellucci and N. Parravano showed that the potassium salts of plumbic, stannic, and platinic acids are isomorphous. H. Reihlen and W. Hühn discussed the optical activity of some ammino-salts. There are also the hydrochloroplatinous acids described by L. Wöhler and F. Martin—tetrachloroplatinous acid, H_2PtCl_4; the doubtful pentachloroplatinous acid, H_2PtCl_5, thought to be a derivative of $PtCl_3$-platinum tervalent; and hexachloroplatinic acid, H_2PtCl_6; and platinic acid, H_2PtO_4—a derivative of platinum trioxide. F. Martin, and L. Wöhler and F. Martin showed that in the trioxide platinum is probably *sexivalent*. P. C. Ray and S. C. S. Gupta suggested that the mercaptidochloride, $PtCl(C_2H_5)_2S_2$, contains *quinquevalent platinum*:



and examples were also given by P. C. Ray and N. N. Ghosh. W. Pullinger suggested that platinum is *octovalent* in the compound $PtCl_2.2COCl_2$:

$$O{=}Pt{\lessdot}^{O}_{O} \qquad\qquad Cl_6{\equiv}Pt{<}^{CO}_{CO}$$

Platinum sexivalent **Platinum octovalent**

R. C. Menzies, L. A. Tschugaeff, I. I. Tschernaieff, P. T. Cleve, S. M. Jörgensen, C. W. Blomstrand, A. Werner, F. M. Jäger, J. Piccard and J. H. Dardel, A. F. Richter, H. Reihlen and co-workers, H. Remy, A. P. Smirnoff, and E. G. Cox and co-workers, studied the co-ordination and stereochemistry of the platinum salts.

The atomic weight of platinum approximates 195. This is in agreement with the sp. ht. rule; with the isomorphism rule—*vide supra;* and with the usual location of the metal in the periodic table. The position of platinum in the periodic table was discussed by R. Abegg,[2] E. Q. Adams, U. Alvisi, T. Bailey, G. H. Bailey and T. C. Lamb, H. Bassett, E. Baur, A. E. de Chancourtois, L. de Boisbaudran and A. de Lapparent, A. van den Broek, T. Carnelley, R. M. Deeley, J. Delauney, J. Delauney and M. Garnier, G. Errèra, L. R. Gibbes, A. J. Hopkins, J. L. Howe, J. Königsberger, S. M. Losanitsch, R. Lorenz, F. H. Loring, D. I. Mendeléeff, J. Monckman, J. A. R. Newlands, W. Preyer, D. Radulescu, J. W. Retgers, G. Rudorf, J. R. Rydberg, W. Sander, K. Scheringa, K. Schirmeisen, E. Schulze, E. von Stackelberg, G. Tammann, J. Thomsen, B. N. Tschitscherin, F. P. Venable, A. Vosmaer, J. Walker, G. Wendt, A. Werner, and C. Zengelis.

Some attempts were made by J. J. Berzelius [3] in 1813, by L. N. Vauquelin, and by E. Davy in 1817 to determine the atomic weight of platinum. J. J. Berzelius' analysis of platinous chloride furnished 194·7 for the atomic weight of platinum, and later, he analyzed potassium chloroplatinate, and obtained 198·3 from the ratio $K_2PtCl_6 : 4Cl$; 196·6 from the ratio $K_2PtCl_6 : 2KCl$; 197·4 from the ratio $K_2PtCl_6 : Pt$; and 197·1 from the ratio $2KCl : Pt$. These results were supported by the values 197·68 to 198·12 reported by T. Andrews to be derived from a determination of the platinum and chlorine in potassium chloroplatinate dried at 105°. J. S. Stas emphasized the difficulty involved in removing the last traces of water from this salt.

The atomic weights obtained by J. J. Berzelius, and T. Andrews are far too high, and they are generally rejected from the computation of average values. In 1881, K. Seubert showed that the value is nearer 195 than 197, for he calculated 195·13 from the ratio $(NH_4)_2PtCl_6 : Pt$; 197·22 from $(NH_4)_2PtCl_6 : 6AgCl$; 194·83 from $K_2PtCl_6 : Pt$; 195·06 from $K_2PtCl_6 : 2KCl$; and 195·31 from $K_2PtCl_6 : 4AgCl$. These results were confirmed by those of W. Halberstadt, who obtained 194·65 from the ratio $PtBr_4 : Pt$; 194·87 from $(NH_4)_2PtBr_6 : Pt$; 195·08 from $K_2PtBr_6 : Pt$; 195·78 from $K_2PtBr_6 : 2KBr$; 195·01 from $(NH_4)_2PtCl_6 : Pt$; 194·75 from $K_2PtCl_6 : Pt$; and 195·29 from $K_2PtCl_6 : 2KCl$. The analyses of potassium chloroplatinate by W. Dittmar and J. McArthur involve corrections for some hydroxyl replacing chlorine, and hydrogen replacing potassium, and they calculated 195·50 from the ratio $2KCl : Pt$. F. Schulz obtained 194·5 from five analyses of ammonium chloroplatinate.

E. H. Archibald obtained values based on analyses of potassium and ammonium chloroplatinates and bromoplatinates. The analyses of potassium chloroplatinate furnish 195·213 from the ratio $K_2Cl_6 : Pt$; 195·219 from $4AgCl : Pt$; 195·236 from $2AgCl : Pt$; 195·228 from $4AgCl : K_2PtCl_6$; 195·274 from $2AgCl : K_2PtCl_6$; 195·220 from $4Ag : Pt$; 195·233 from $2Ag : Pt$; 195·208 from $4Ag : K_2PtCl_6$; and 195·252 from $2Ag : K_2PtCl_6$. The analyses of potassium bromoplatinate furnish 195·221 from the ratio $K_2Br_6 : Pt$; 195·225 from $4AgBr : Pt$; 195·222 from $2AgBr : Pt$; 195·238 from $4AgBr : Pt$; 195·238 from $2AgBr : K_2PtBr_6$; 195·220 from $4Ag : Pt$; 195·224 from $2Ag : Pt$; 195·220 from $4Ag : K_2PtBr_6$; and 195·242 from $2Ag : K_2PtBr_6$. The analyses of ammonium chloroplatinate

furnished 195·191 from the ratio $(NH_4)_2PtCl_6 : Pt$; 195·216 from $6AgCl : Pt$; 195·245 from $6AgCl : (NH_4)_2PtCl_6$; 195·213 from $6Ag : Pt$; and 195·241 from $6Ag : (NH_4)_2PtCl_6$. The analyses of ammonium bromoplatinate furnished 195·206 from the ratio $(NH_4)_2PtBr_6 : Pt$; 195·214 from $6AgBr : Pt$; 195·242 from $6Ag : (NH_4)_2PtBr_6$; 195·220 from $6Ag : Pt$; and 195·244 from $6Ag : (NH_4)_2PtBr_6$. The best representative value from E. H. Archibald's determinations is 195·22.

The international standard for the best representative value of the atomic weight of platinum for 1931 is 195·2, and representative values were discussed by F. W. Clarke, L. Meyer and K. Seubert, J. D. von der Plaats, W. M. Watts, T. W. Richards, W. A. Noyes, G. D. Hinrichs, and A. Vürtheim.

C. T. Heycock and F. H. Neville [4] discussed the molecular state of platinum in alloys with cadmium, lead, and bismuth; and E. O. von Lippmann estimated 30 to 40 atoms per molecule. W. C. Roberts-Austen added that experiments on the diffusion of platinum suggested that the molecules are more complex than those of silver, or gold. The relations between the elements and their at. wts. were discussed by G. Osann, M. Gerber, F. Sanford, and C. A. Martius; the relations between the at. wts. and the affinities of the elements, by E. Donath and J. Mayrhofer, P. Pfeiffer, and F. Gramp; between the at. wts. and the heats of reaction, by M. Berthelot; the relations between the at. wts. and the elastic constants, by J. Johnston; and the relations between the at. wts. and the colour of the elements, by M. C. Lea.

The **atomic number** of platinum is 78. E. Amaldi,[5] A. J. Dempster, B. Fuchs and H. Kopfermann, H. Kopfermann and K. Krebs, B. Jaeckel and H. Kopfermann, F. Allison and E. J. Murphy, and B. Venkatesachar and L. Sibaiya reported that platinum has five **isotopes** of atomic mass 192, (193), 194, 195, and 196 with the relative abundances, for the 192, 194, 195, and 196 isotopes are, respectively, 2, 10, 13, 16; J. H. Bartlett studied the subject. The **atomic disruption** of platinum by the bombardment of α-particles has not been noted by E. Rutherford and J. Chadwick, or by H. Pettersson and G. Kirsch; J. M. Cork and E. O. Lawrence, and A. Matzner observed the atomic disintegration of platinum by bombardment with neutrons; G. Kirsch found that with α-rays from polonium, disintegration occurs; and G. I. Pokrovsky said that the platinum becomes radioactive. According to N. Bohr, and E. C. Stonier, the **electronic structure** of platinum is (2) for the K-shell; (2, 2, 4) for the L-shell; (2, 2, 4, 4, 6) for the M-shell; (2, 2, 4, 4, 6, 6, 8) for the N-shell; (2, 2, 4, 4, 4) for the O-shell; and (2) for the P-shell. S. K. Allison, A. E. van Arkel and J. H. de Boer, E. Bose, J. Chadwick, J. A. Crowther, F. Deininger, H. Eyring and A. Sherman, P. D. Foote, M. Kahanovicz, S. Kato, W. Meier, B. V. Nekrasoff, C. D. Niven, J. Patterson, H. Perlitz, R. Pohl, G. I. Pokrovsky, P. Ray, O. W. Richardson, W. Hume-Rothery, H. J. Walke, and H. A. Wilson made estimates of the number of electrons per atom of platinum.

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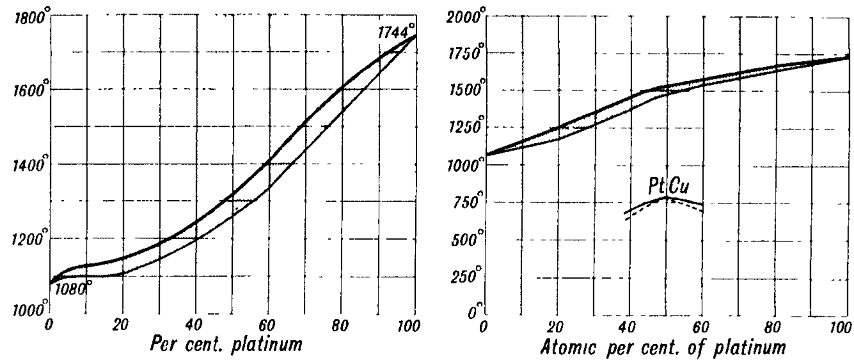
§ 16. Intermetallic Compounds, and Alloys of Platinum

J. Dewar and A. Scott [1] observed that platinum is very strongly attacked by the vapour of the alkali metals. According to H. Davy, **platinum-potassium alloys** are readily formed since the two metals when heated together unite with incandescence, forming a brittle, shining mass. H. Davy observed that the alloy of potassium and platinum burns when heated in air, forming a yellow powder which gives off oxygen when heated, and is decomposed by water. K. A. Hofmann and H. Hiendlmaier observed that if potassium is melted with platinum in air, the product passes into soln. as potassium platinate. H. Davy likewise prepared **platinum-sodium alloys.** C. T. Heycock and F. H. Neville observed that platinum is insoluble in molten sodium. J. Dewar and A. Scott noted that platinum is attacked by the vapour of sodium, and V. Meyer added that sodium vapour, in nitrogen, begins to attack platinum at a red-heat, and the attack is greater, the higher the temp. F. Haber and M. Sack, and M. Sack observed that platinum takes up sodium when heated to redness in the vapour of the alkali metal, and when the metal is afterwards treated with water, it becomes loose and porous on the surface. According to A. Brester, a sodium-platinum alloy is formed by the electrolysis of sodium sulphate with a platinum cathode. P. G. Ehrhardt found that **platinum-lithium alloys** are harder than platinum itself.

According to A. F. Gehlen,[2] **platinum-copper alloys** are readily formed at a white-heat; and E. D. Clarke obtained the alloy by melting equal weights of the two metals in the oxyhydrogen flame. H. le Chatelier observed that at its m.p., copper gives off sufficient vapour to corrode platinum. Alloys were also made by C. S. Brainin, C. Winkler, J. Murray, C. Barus, and F. Doerinckel. According to C. Krug, the two metals form alloys in all proportions. E. M. Wise and coworkers studied the use of the platinum-copper alloys for dental purposes. B. N. Sen discussed the diffusion of copper into platinum. The f.p. curve, Fig. 29, falls continuously from the m.p. of platinum to that of copper, and there is therefore a continuous series of solid soln. As pointed out by G. Tammann, no compound appears on the curve although C. Krug was under the impression that a **platinum cupride,** PtCu, is formed. The subject was discussed by K. Bornemann, E. Jänecke,

K. Honda and T. Ishigaki, J. A. M. van Liempt, C. Barus, W. Guertler, and A. von der Ropp. N. S. Kurnakoff and V. A. Nemiloff observed the f.p. curves, Fig. 30, and found that solid alloys exhibit recalescence between 700° and 800° with a maximum of 850° with alloys having 50 at. per cent. of platinum. This indicates the formation of the PtCu-compound, and this is confirmed by measurements



FIGS. 29 and 30.—The Freezing Points of Platinum-Copper Alloys.

of the hardness (Fig. 31), conductivity, and temp. coeff. of the conductivity (Fig. 32) of re-heated and tempered alloys. H. Röhl discussed the elastic properties of the Cu_3Pt alloy.

G. Natta, and C. Matano studied the diffusion of platinum in copper. According to C. Krug, alloys with 4 per cent. of platinum are rose-red; with 10 to 12 per cent., bronze colour; with 15 to 20 per cent., gold-yellow; with 50 per cent.,

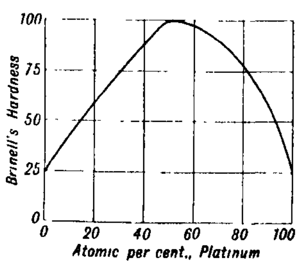


FIG. 31.—The Hardness of the Pt–Cu Alloys.

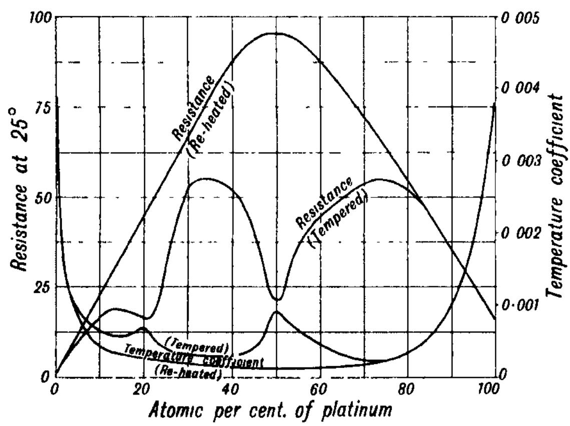


FIG. 32.—The Resistance and Temperature Coefficient of the Pt–Cu Alloys.

pale grey; and with 75 per cent., it is difficult to distinguish the colour from that of platinum itself. F. Doerinckel said that alloys with over 40 per cent. of platinum are white; A. F. Gehlen that alloys with 3·7 per cent. of platinum are rose-red; and E. D. Clarke, that alloys with 50 per cent. of platinum are golden yellow. A. F. Gehlen said that the alloy with 3·7 per cent. of platinum had a fine-grained structure. H. Behrens observed that when polished surfaces are etched with nitric acid, deep furrows are cut between cushion-like crystals. W. Lewis found the sp. gr. of alloys with platinum and

Copper .	0·969	66·7	80	83·3	88·9	92·3	96·15	100 per cent.
Sp. gr. .	11·400	10·410	9·908	9·693	9·300	9·251	8·970	8·830

W. Biltz and F. Weibka studied the at. vol. F. Doerinckel said that the alloys are soft and tough; and that the hardness is between 3 and 4 on Mohs' scale. F. E. Carter's values for Brinell's hardness of workable alloys are given in Table IV.

TABLE IV.—BRINELL'S HARDNESS OF PLATINUM ALLOYS.

Alloy	Percentage amount			
	5	10	15	20
Ir	80	105	140	175
Os	117	175	—	—
Pd	65	70	73	75
Rh	67	73	77	80
Ru	105	158	—	—
Au	102	148	—	—
Ag	80	125	170	172
Cu	110	135	142	145
Ni	138	195	236	270

A. F. Gehlen said that the alloy with 3·7 per cent. of platinum is malleable, and E. D. Clarke that the 50 : 50-alloy has a sp. gr. like gold, is malleable, and easily filed. F. E. Carter said that with up to 10 per cent. of copper, the alloys do not blacken on heating, but with more copper they do blacken and become difficult to work. Alloys with up to 30 per cent. of copper may be hot rolled, but beyond that, the alloys are hard and brittle. C. Krug observed that alloys with over 10 per cent. of platinum are liable to "spitting" when they solidify. C. H. Johansson and J. O. Linde examined the X-ray spectrum. H. J. Seemann, and C. Barus, and E. Sedström measured the sp. resistance and its temp. coeff. F. E. Carter said that the addition of copper to platinum raises the electrical resistance very markedly; the resistance R ohms, the temp. coeff. a per c.c., and the thermal e.m.f. against platinum at 1100°, are:

Copper .	5	10	15	20	25	30 per cent.
R . .	227	335	430	540	530	500
a . .	0·00015	0·00015	0·00015	0·00016	0·00012	—
E.m.f. .	+3·48	+5·05	--	+0·80	—	−5·05

C. S. Brainin patented an alloy with about 25 per cent. of copper for use as high-resistance wires. N. S. Kurnakoff and V. A. Nemiloff's results are summarized in Fig. 32. H. le Chatelier found the thermoelectric force of platinum against an alloy with 5 per cent. of copper to be $E=1{\cdot}3\theta-0{\cdot}0024\theta^2$ between 0° and 1500°. E. Sedström studied the subject; and G. Tammann and H. Wiederholdt, the polarization of the alloy; and E. Vogt, and H. J. Seemann, the magnetic properties of the alloys.

A. Sieverts and co-workers observed that platinum raises the solubility of hydrogen in molten copper. E. D. Clarke said that the 50 : 50-alloy is tarnished in air; and C. Krug noted that the alloys generally resist atmospheric corrosion very well. A. Sieverts and E. Bergner found that platinum lowers the solubility of sulphur dioxide in copper. F. Doerinckel, and H. Behrens noted that alloys with up to 50 per cent. of platinum are etched by nitric acid. According to C. Winkler, alloys with [Cu] per cent. of copper, yield [Pt] per cent. of platinum when treated with nitric acid:

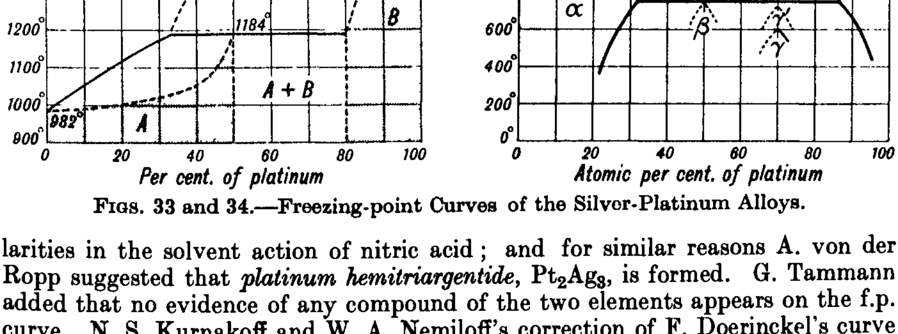
HNO_3 sp. gr.	1·398		1·298		1·190		1·298 (fuming)		
[Cu] . .	90·24	99·00	89·89	98·85	90·61	99·00	89·80	94·78	per cent.
[Pt] . .	45·60	52·00	26·57	41·27	11·19	37·03	51·16	40·81	,,

C. Krug said that the solubility of platinum is not influenced by the concentration or proportion of the acid employed, but it is affected by the duration of the action; and since a portion of the copper always remains associated with the platinum,

he assumed that the insoluble part is a chemical compound. G. Tammann's study of the action of gold chloride, nitric acid sp. gr. 1·44, fuming hydrochloric acid, palladium chloride, ferric chloride, cupric chloride, mercurous nitrate, ammonium sulphide, and sodium sulphide indicated a limit with alloys having up to 32 per cent. of platinum.

J. P. J. d'Arcet [3] prepared **platinum-silver alloys** by melting the component metals together. H. le Chatelier observed that molten silver at its m.p. gives off enough vapour to attack platinum. F. E. Carter said that silver rapidly hardens platinum, and alloys used in dentistry, and in making electrical contacts are fairly ductile. The so-called *dental alloys*, first and second qualities, contain, respectively, 66 and 75 per cent. of silver—the remainder being platinum. Some alloys containing 51 to 62 per cent. of tin, 30 to 46 per cent. of silver, 1·3 to 5·8 per cent. of gold, and 0·4 to 1·6 per cent. of platinum, are, according to E. A. Smith, used in the preparation of dental amalgam. The silver-platinum dental alloys were studied by E. M. Wise and co-workers.

J. Murray, H. Rössler, C. Winkler, F. Doerinckel, J. F. Thompson and E. H. Miller, A. von der Ropp, and V. Strouhal and C. Barus obtained the alloys by melting the constituent metals either in the blast-gas flame, the oxyhydrogen flame, or in high temp. furnaces. W. Truthe studied the effect of silver on platinum in cupellation. W. Spring noted that when platinum electroplated with silver is drawn into wire, the metals alloy under the severe press. E. Priwoznik obtained the alloy by igniting silver nitritoplatinite. H. Rössler said that the two metals form alloys in all proportions, but F. E. Carter said that the alloys do not form a continuous series of solid soln. as in the case of platinum alloyed with gold, or palladium with silver. The metals do not readily dissolve in one another, and they tend to separate on cooling. J. Prinsep attempted to measure the m.p. of silver-platinum alloys by a gold air thermometer; and to use the alloys as pyroscopes. C. T. Heycock and F. H. Neville observed that adding 3·55 per cent. of platinum to silver raised the f.p. to 990°. F. Doerinckel found that a series of solid soln. is formed with from 0 to 48 per cent. of platinum; the composition of the end-member of the series is *platinum diargentide*, $PtAg_2$, but it is not considered to be a chemical individual. Above 1184°, it decomposes into crystals rich in platinum, and a fused mass with about 32 per cent. of platinum. J. F. Thompson and E. H. Miller thought it possible that a compound is formed because of some irregu-



FIGS. 33 and 34.—Freezing-point Curves of the Silver-Platinum Alloys.

larities in the solvent action of nitric acid; and for similar reasons A. von der Ropp suggested that *platinum hemitriargentide*, Pt_2Ag_3, is formed. G. Tammann added that no evidence of any compound of the two elements appears on the f.p. curve. N. S. Kurnakoff and W. A. Nemiloff's correction of F. Doerinckel's curve is shown in Fig. 33, where *A* represents a solid soln. of platinum in silver; *B*, a

solid soln. of silver in platinum ; and $A+B$, a mixture of the two solid soln. Observations on the subject were made by W. Guertler, G. Natta, K. Bornemann, and E. Jänecke. C. H. Johansson and J. O. Linde's results are summarized in Fig. 34, where the Greek letters refer to solid soln.

According to J. F. Thompson and E. H. Miller, under the microscope, the alloy with 10·39 per cent. of platinum consists of crystals set in a non-composite ground mass. On cooling from 1200°, a development of heat was observed at 1045° to 1050°, and a much larger development at 1000°. The alloy containing 20·59 per cent. platinum, when cooled from 1100°, developed heat at 1085° and possibly also at 995°. The microstructure showed large, white dendrites in a non-composite ground mass. The alloy containing 31·46 per cent. platinum, on cooling from 1300°, gave marked but irregular developments of heat between 1170° and 1100°. The structure consisted of grey crystals in a dark ground mass. The alloy containing 37·89 per cent. platinum resembled the 31·46 per cent. alloy in structure, but gave sharp developments of heat at 1240° and 1170°. The alloy containing 57·05 per cent. platinum also resembled the 31·46 per cent. alloy in structure; on cooling from 1400°, it gave developments of heat at 1240°, 1180°, and 1090°. K. Gebhard and H. J. Wiester studied the recrystallization of the platinum-silver alloys. C. H. Johansson and J. O. Linde's results for the lattice constant of the alloys are summarized in Fig. 35. The results for the dotted lines

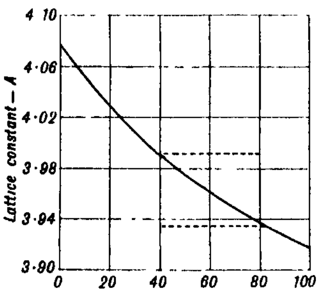


FIG. 35.—The Lattice Constants of the Platinum-Silver Alloys.

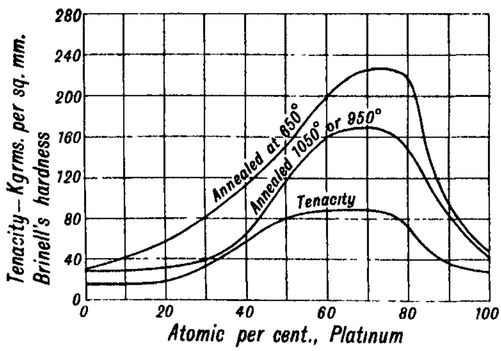


FIG. 36.—The Hardness and Tenacity of Platinum-Silver Alloys.

refer to solid soln. The alloys for up to about 30 per cent. platinum were quenched from 750° to 850°, and those above 50 at. per cent. platinum were quenched from 1150°. The X-radiograms were studied by J. Weerts. The sp. gr. referred to water at 4° is :

Platinum .	0	10·39	20·59	31·46	37·89	57·05 per cent.
Sp. gr. .	10·61	11·17	11·80	12·57	13·19	14·25

W. Lewis gave for the sp. gr. of alloys with

Silver .	50	66·7	75	87·5	100 per cent.
Sp. gr. .	13·535	12·452	11·790	10·867	10·980

W. Biltz and F. Weibka studied the at. vol. J. P. J. d'Arcet observed that the alloys of platinum with silver are less white, less malleable, and less hard than silver, and when quietly fused, an alloy richer in platinum collects at the bottom. C. Winkler obtained analogous results. J. F. Thompson and E. H. Miller observed that alloys with over 30 per cent. of platinum are much harder than those with a lower proportion of platinum, and the hardness increases as the proportion of platinum increases; and F. Doerinckel added that alloys with up to 30 per cent. of platinum are scarcely harder than their components, but beyond that point the hardness increases, and an alloy with 70 per cent. of platinum is rather harder

than calcite. N. S. Kurnakoff and W. A. Nemiloff's measurements of Brinell's hardness of alloys annealed at 650°, and at 950° to 1050°, and of the tensile strength in kgrms. per sq. mm. are summarized in Fig. 36—*vide* Table IV. W. Geibel's measurements of the tensile strength of 1 mm. wires are summarized in Fig. 37. These alloys were used by H. Bush for hooks and rivets.

A. Matthiessen found the linear thermal expansion of alloys with 66 per cent. of silver to be $l=l_0(1+0{\cdot}0_41415\theta+0{\cdot}0_7107\theta^2)$; and the cubic expansion $v=v_0(1+0{\cdot}0_442246\theta+0{\cdot}0_7322\theta^2)$. F. A. Schulze gave for the thermal conductivity, k,

Platinum .	0	10	25	30	33 per cent.
k . . .	1·08	0·98	0·38	0·31	0·30

J. F. Thompson and E. H. Miller noted that alloys with over 40 per cent. of silver do not spit perceptibly on solidification. E. Hagen and H. Rubens measured the emissivity of the alloys; and H. Weisz found that platinum acts as a nucleus for the solarization of silver bromide films in photography.

A. Matthiessen and C. Vogt found that the curve for the electrical conductivity has a break for alloys with 33 per cent. of platinum. The conductivity

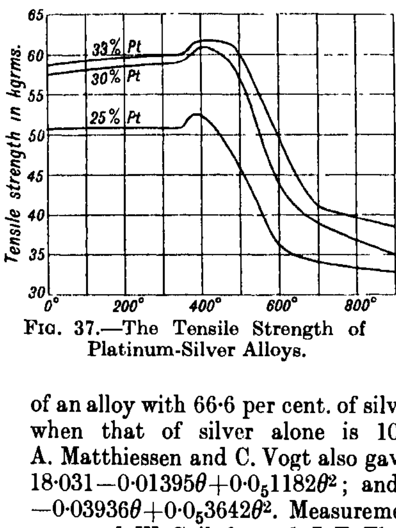


Fig. 37.—The Tensile Strength of Platinum-Silver Alloys.

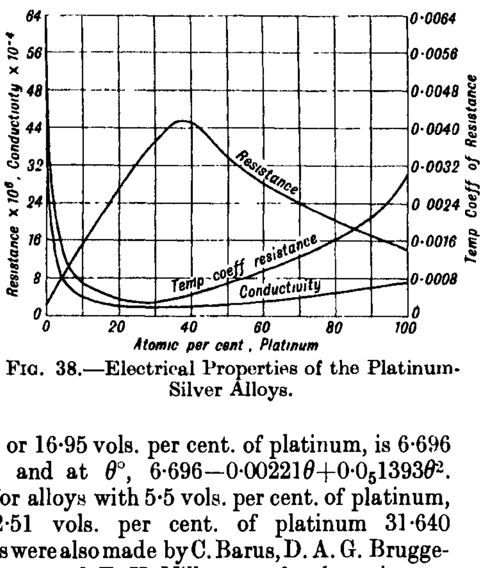


Fig. 38.—Electrical Properties of the Platinum-Silver Alloys.

of an alloy with 66·6 per cent. of silver, or 16·95 vols. per cent. of platinum, is 6·696 when that of silver alone is 100; and at $\theta°$, $6{\cdot}696-0{\cdot}00221\theta+0{\cdot}0_513930\theta^2$. A. Matthiessen and C. Vogt also gave for alloys with 5·5 vols. per cent. of platinum, $18{\cdot}031-0{\cdot}013956\theta+0{\cdot}0_511182\theta^2$; and 2·51 vols. per cent. of platinum $31{\cdot}640-0{\cdot}039336\theta+0{\cdot}0_536420\theta^2$. Measurements were also made by C. Barus, D. A. G. Bruggeman, and W. Geibel; and J. F. Thompson and E. H. Miller gave for the resistance in ohms, R,

Platinum . .	0	10·39	20·59	31·46	37·89 per cent.
R	0·0217	0·0918	0·1814	0·2914	0·3110

J. Dewar and J. A. Fleming gave for an alloy with 66 per cent. of silver,

	99·3°	18·35°	1°	−80°	−100°	−182°
R .	$0{\cdot}0_427400$	$0{\cdot}0_426905$	$0{\cdot}0_426824$	$0{\cdot}0_426311$	$0{\cdot}0_426108$	$0{\cdot}0_425537$

N. S. Kurnakoff and W. A. Nemiloff's measurements of the sp. resistance, $R\times10^6$, of the sp. conductivity, $K\times10^{-4}$, and of the temp. coeff. of the resistance between 25° and 100° are summarized in Fig. 38, and those of C. H. Johansson and J. O. Linde in Fig. 39. P. Wenke and M. Wien studied the effect with thin films. Observations on the temp. coeff. were made by C. Barus, C. G. Knott and J. G. McGregor, H. Chevallier, and F. Uppenborn. The effect of an alternating current was studied by R. S. Willows; the effect of torsion, by H. Tomlinson, and J. Klemencic; and

a comparison of the ratio of the thermal, k, and the electrical, K, conductivities at 25°, by F. A. Schulze.

Platinum . . .	0	10	25	30	33 per cent.
$K \times 10^4$ . . .	57·35	12·72	4·23	3·22	3·05
$k/K \times 10^7$ . . .	69	77	90	95	106

W. Geibel's results for the thermoelectric force of platinum, E millivolts, against platinum-silver alloys are indicated in Fig. 40; and those of C. H. Johansson and J. O. Linde for the platinum-silver alloys against silver, at 18°, in Fig. 41. Observations were also made by A. W. Smith, W. H. Keesom and J. N. van Ende, C. G. Knott and J. G. McGregor, W. Broniewsky, V. Strouhal and C. Barus, and H. Tomlinson; and the thermoelectric force against copper was measured by J. Klemencic. F. Braun observed that when spluttered by a current from a Leyden jar, the alloy separates into its constituents. D. A. G. Bruggeman studied the dielectric constants.

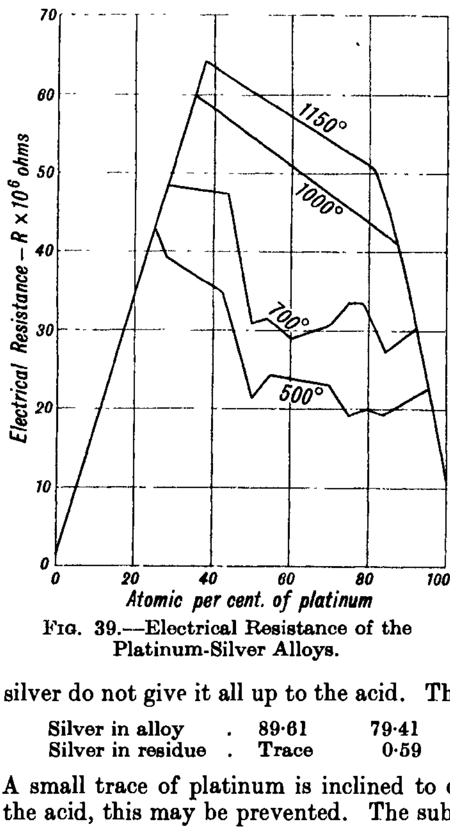


FIG. 39.—Electrical Resistance of the Platinum-Silver Alloys.

F. E. Carter observed that even but a few per cent. of platinum in silver reduces the rate of tarnishing of the silver. According to J. P. J. d'Arcet, sulphuric acid dissolves only silver from platinum silver alloys. J. F. Thompson and E. H. Miller found that all the silver is dissolved only from alloys containing 90 per cent. or more silver; alloys with less silver do not give it all up to the acid. Thus,

Silver in alloy .	89·61	79·41	68·54	62·11	42 95 per cent.
Silver in residue .	Trace	0·59	0·98	2·24	2·70 ,,

A small trace of platinum is inclined to dissolve with the silver, but by diluting the acid, this may be prevented. The subject was also studied by H. Carmichael;

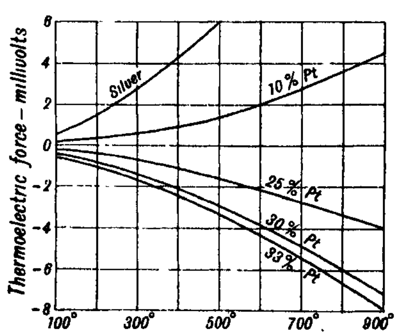


FIG. 40.—Thermoelectric Properties of the Platinum-Silver Alloys against Platinum.

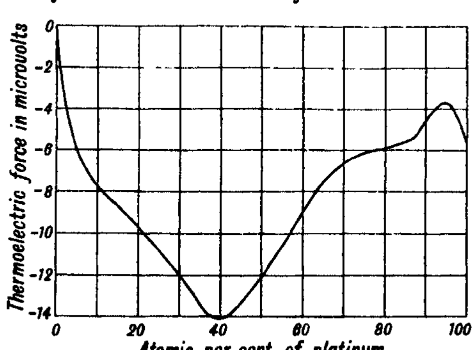


FIG. 41.—Thermoelectric Properties of the Platinum-Silver Alloys against Silver.

and A. Steinmann recommended the use of a soln. of 100 vols. of acid and 22 vols. of water for dissolving out the silver, the operation being twice repeated at 240°.

K. Hradecky observed that selenic acid dissolves silver from these alloys yielding a residue of platinum.

F. Doerinckel observed that dil. nitric acid attacks the alloys with increasing difficulty as the proportion of platinum increases; and when 50 per cent. of platinum is present the alloy is etched only slightly. An alloy with 60 per cent. of platinum, and rapidly cooled from the molten state, is readily attacked by conc. nitric acid, but if the alloy has been annealed for 6 hrs. at 1180°, it is much more resistant. C. von Sickingen, and J. P. J. d'Arcet observed that although platinum is not attacked by nitric acid, yet it dissolves slightly when its alloys with silver are treated with that acid. H. How, and E. Priwoznik considered the solubility of the platinum to be connected with the formation of a silver nitritoplatinite. The solubility of the platinum in nitric acid was also observed by H. Debray, J. E. Herberger, P. Johnson, J. W. Mallet, H. Miller, A. D. van Riemsdyk, W. J. Sharwood, and H. N. Warren. C. Winkler, and A. von der Ropp showed that the conc. of the acid is of importance. According to J. Spiller, nitric acid of sp. gr. 1·42 will dissolve 0·75 to 1·25 per cent. of platinum from its alloy with 12 times its weight of silver, whilst treatment with a more conc. acid is attended by the separation of platinum black. A less conc. acid dissolves less platinum. J. F. Thompson and E. H. Miller observed that alloys with less than 20 per cent. of silver furnish a colloidal, dark brown sol of platinum, which, after standing several days, flocculates and deposits the platinum as a black powder in a very fine state of subdivision, and leaves a colourless soln of the silver salt. According to A. von der Ropp, the residual platinum explodes when dried on a filter, and heated to about 200°. C. Winkler found that [Pt] per cent. of platinum is dissolved from alloys with [Ag] per cent. of silver:

HNO_3 sp. gr.	1·398		1·298		1·190		1·298	
[Ag]	90·83	99·24	90·24	99·05	89·84	98·96	90·44	94·92
[Pt]	56·95	75·00	44·43	70·00	69·33	75·86	37·45	35·23

J. F. Thompson and E. H. Miller found that with nitric acid of sp. gr. 1·10, the following proportions of platinum passed into soln. from 100 parts of alloy:

Platinum	Alloy	10·39	20·59	31·46	37·89	57·05 per cent.
	Residue	3·59	6·77	24·50	35·49	52·97 ,,
	Dissolved	6·80	13·82	6·96	2·40	4·08 ,,

The results are irregular, but they are taken to prove that, in assaying, platinum cannot be satisfactorily separated by nitric acid from its alloy with silver. I. Koifman obtained analogous results with alloys, containing 0·219 to 5·162 per cent. of platinum. J. E. Herberger observed that aqua regia extracts the platinum from the alloys and converts the silver into chloride. G. Tammann's study of the action of gold chloride, nitric acid sp. gr. 1·44, fuming hydrochloric acid, ferric chloride, and ammonium sulphide indicated a limit of reactivity with up to 35 per cent. of platinum. J. W. Mallet found that an alloy with 31·09 per cent. of platinum, at ordinary temp., gradually absorbs five times its weight of mercury and becomes very brittle. E. Jänecke constructed the diagram, Fig. 42, for **platinum-silver-copper alloys,** showing the eutectic line, and the region of solid soln.

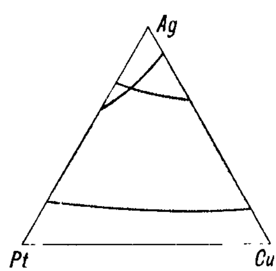
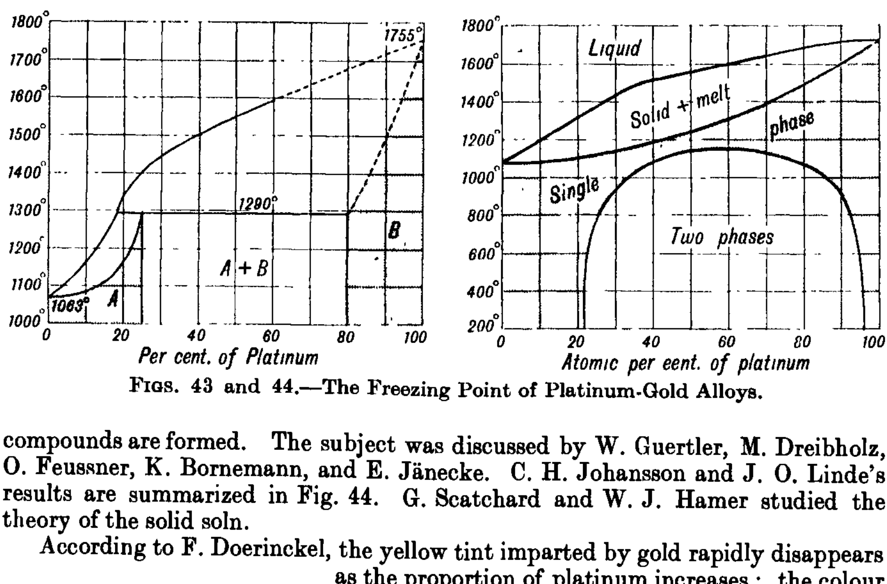


FIG. 42.—The Ternary System: Pt–Ag–Cu.

J. Prinsep,[4] C. Hatchett, J. Murray, J. O. Whiteley, and E. D. Clarke prepared some **platinum-gold alloys;** and alloys were also obtained by melting the constituent metals in the oxyhydrogen flame or in a high temp. furnace, by T. Erhard and A. Schertel, C. Barus, and F. Doerinckel. J. Weineck rolled gold-plated platinum; and J. W. Pratt noticed that an alloy is formed when gold chloride is heated above its m.p. in a platinum vessel. E. M. Wise

and J. T. Eash, and H. Bush recommended the alloys for artificial teeth; and dental alloys of these two metals were studied by E. M. Wise and co-workers. J. Prinsep attempted to measure the m.p. of gold-platinum alloys by a gold air thermometer, and to use the alloys as pyroscopes. W. Truthe studied the effect of platinum on gold in cupellation; and E. Matthey, the liquation of the alloys. K. Fischbeck, A. Jedele, and W. Jost studied the rate of diffusion of platinum in gold. F. Doerinckel found that alloys of gold with up to 60 per cent. of platinum from a continuous series of solid soln., and that there is a considerable interval of temp. between the liquidus and solidus curves. W. Stenzel and J. Weerts found that the solubility of platinum in gold at 1100°, 900°, and 700° is 43, 30, and 25 at. per cent., and that of gold in platinum, 19, 7, and 3·5 at. per cent., respectively. F. Doerinckel's diagram modified by A. T. Grigoréeff is given in Fig. 43. The region *A* represents a solid soln. of platinum in gold; *B*, a solid soln. of gold in platinum; and *A*+*B*, a mixture of the two solid soln. G. Tammann said that no



FIGS. 43 and 44.—The Freezing Point of Platinum-Gold Alloys.

compounds are formed. The subject was discussed by W. Guertler, M. Dreibholz, O. Feussner, K. Bornemann, and E. Jänecke. C. H. Johansson and J. O. Linde's results are summarized in Fig. 44. G. Scatchard and W. J. Hamer studied the theory of the solid soln.

According to F. Doerinckel, the yellow tint imparted by gold rapidly disappears as the proportion of platinum increases; the colour of an alloy with 10 per cent. of platinum is much paler than that of gold; with 30 per cent. of platinum, the yellow tinge of gold is just perceptible; and with 40 per cent. of platinum, the colour is the same as that of platinum. C. Hatchett said that the alloy of 1 part of platinum and 11 of gold is greyish-white; L. B. G. de Morveau, that the alloy with 15·5 per cent. of platinum is gold coloured; M. H. Klaproth, that alloys with Au : Pt exceeding 8 are gold coloured; L. Gilbert, that the colour of an alloy with 1 per cent. of platinum is indistinguishable from that of gold; and E. D. Clarke, that the alloy with 1 part of platinum to 9·6 of gold is almost the colour of gold. T. Erhard and A. Schertel observed that rapidly cooled alloys have a fine crystalline structure, and, slowly cooled alloys,

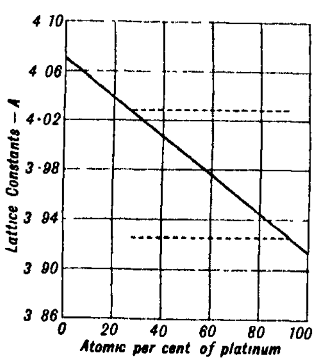


FIG. 45.—The Lattice Constants of the Gold-Platinum Alloys.

a coarse crystalline structure. C. H. Johansson and J. O. Linde's results for the lattice-constants are summarized in Fig. 45. The alloys with 40 to 100 at. per cent. of platinum were quenched from 1200°, and those with 0 to 32 at. per cent.

of platinum, from 1000°. The results represented by the dotted lines were with samples quenched at 800°. W. Stenzel and J. Weerts found that the lattice parameter of quenched homogeneous alloys is a linear function of the composition. W. Lewis gave for the sp. gr. of the binary alloys from platinum of sp. gr. 19·285:

Gold .	66·7	75·0	83·3	91·67	93·75	95·8	97·0	98·0	99·0
Sp. gr. .	18·378	18·613	18·812	18·835	18·918	19·089	19·128	19·262	19·273

F. Doerinckel found that the hardness of an alloy with 10 per cent. of platinum is very like that of gold; with 20 to 30 per cent. of platinum, the same as that of platinum, and with over 50 per cent. of platinum, about the same as that of calcite. The following is a selection from A. T. Grigoréeff's measurements of Brinell's hardness, H, of the cast alloys and of annealed alloys:

Platinum .	0	5	10	20	40	60	80	90	100
H Cast .	—	27·4	33·8	38·2	83·0	127·3	155·3	99·5	—
H Ann. .	13·92	30·2	34·2	37·2	77·7	92·3	128·8	111·4	26·0

The results of C. H. Johansson and J. O. Linde are summarized in Fig. 46—*vide* Table IV—for alloys quenched from 900°; for alloys with 8 to 32 at. per cent. of platinum from 1000°, and with 40 to 96 at. per cent. of platinum from 1175° to 1225°; and alloys annealed at 900°. W. Goedecke studied the change of the hardness during the ageing of the alloys; and P. D. Merica, the precipitation hardness. C. Hatchett found that the alloy with 91·67 per cent. of gold is malleable; and E. D. Clarke, that alloys with 33·3 to 50 per cent. of gold are brittle. F. E. Carter said that the addition of gold rapidly hardens platinum, and that the limit of workability is attained with 10 per cent. of gold. The alloys with gold in excess work satisfactorily, but it is difficult to make them homogeneous. L. Nowack studied the age-hardening of the alloys. W. Geibel found that alloys with up to 20 per cent. of platinum are easy to work, but alloys with 20 to 40 per cent. are difficult. O. Feussner studied the hardening of the alloy by additions of the alkaline earth metals, magnesium, zinc, tin, iron, cobalt, and nickel. The tensile strengths of 1 mm. wires expressed in kgrms. are:

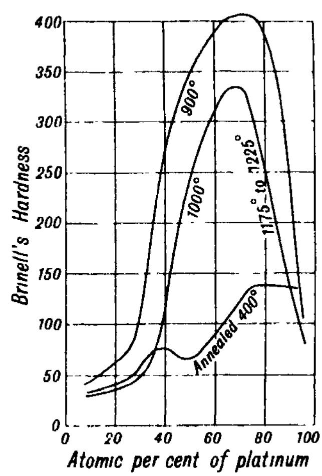


FIG. 46.—Brinell's Hardness of the Platinum-Gold Alloys.

Platinum . .	0	10	20	30	40 per cent.
Tensile strength .	21·5	32	52	58	69 kgrms.

The elastic modulus of an alloy with 77·8 per cent. of gold was found by G. Wertheim to be 9844 kgrms. per sq. mm., and the tensile strength to be 7·12 kgrms. per sq. mm.; he also found the velocity of sound in the alloy to be 6·848 when that in air is unity. F. A. Schulze gave for the thermal conductivity, k,

Platinum . .	0	10	20	30	40 per cent.
k	3·30	0·76	0·41	0·30	0·26

C. H. Johansson and J. O. Linde's results for the thermal conductivity of the alloys are summarized in Fig. 47. F. E. Carter gave for Brinell's hardness H; Ericson's ductility test in mm.; and the resistance R ohms:

Gold	5	10	60	70	80	90 per cent.
H Hard . .	177	222	226	193	158	105
H Annealed .	98	162	174	135	104	61
Ductility . . .	—	—	6·9	9·7	11·3	12·2
R	133	—	156	153	122	70

F. Doerinckel's values for the m.p. are indicated in Fig. 43. T. Erhard and A. Schertel gave:

Pt .	0	5	10	20	40	60	80	100 per cent.
M.p. .	1075°	1100°	1130°	1190°	1320°	1460°	1610°	1775°

Observations on a few isolated alloys were made by P. Silow, Y. Shimizu, J. Prinsep, and A. Heintz. T. Erhard and A. Schertel found that alloys with 15 to 40 per cent. of platinum are inclined to segregation, and similar results were obtained by

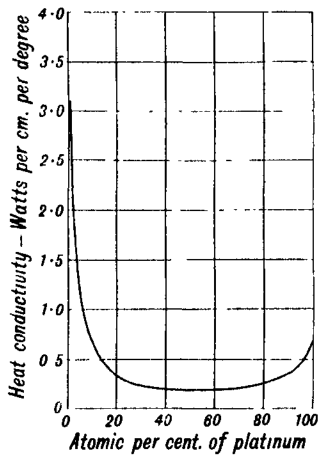


FIG. 47.—The Thermal Conductivity of the Platinum-Gold Alloys.

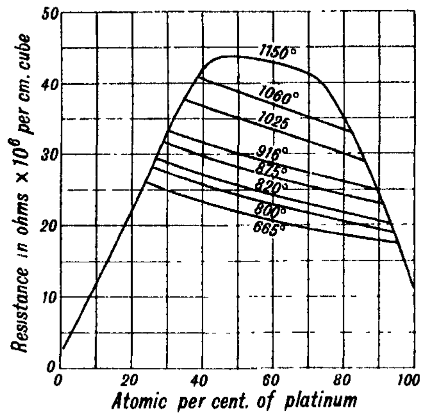


FIG. 48.—The Electrical Resistance of Platinum-Gold Alloys.

H. Seger, and E. Matthey. According to A. D. van Riemsdyk, the presence of 22 thousandths of platinum does not hinder superfusion and flashing in the cupellation of gold. According to W. Geibel, the electrical conductivity, K, at 0°, and the temp. coeff. a, between 0° and 160°, are:

Platinum .	0	10	20	30	40 per cent.
$K\times10^4$.	47·52	9·76	5·57	5·18	3·06
a . .	0·00326	0·00098	0·00054	0·00059	0·00037
$k/K\times10^7$.	71	76	85	86	93

where the ratios of the thermal and electrical conductivities are by F. A. Schulze. C. H. Johansson and J. O. Linde's results are summarized in Fig. 48 for the electrical resistance of alloys quenched from different temperatures. The results within the loop refer to alloys with two phases. C. Barus, and J. O. Linde made observations on the electrical resistance of the alloys. G. Scatchard and W. J. Harmer studied the chemical potentials of liquid and solid solutions of Ag-Pt alloys. W. Geibel found that the thermoelectric force of the alloys against platinum is negative and increases as the proportion of platinum in the alloy is raised. The values become more negative with repeated heating. C. H. Johansson and J. O. Linde's results for the thermoelectric force $E\times10^6$ volts per degree, against gold, at 18°, are indicated in Fig. 49; and the results for the magnetic

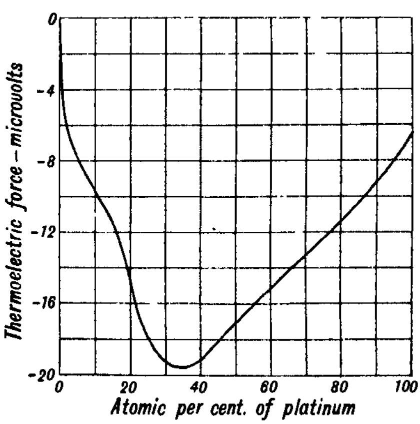


FIG. 49.—The Thermoelectric Force of Platinum-Gold Alloys against Gold.

susceptibility, in Fig. 50. Y. Shimizu studied the effect of stress on the magnetic susceptibility.

P. Johnson found that nitric acid dissolves not only gold but some platinum from the alloys. K. W. Fröhlich discussed the error involved in the determination of platinum when alloys with gold and silver are treated with hot sulphuric acid. Some platinum passes into soln. J. Weineck observed that conc. sulphuric acid, and molten potassium hydroxide with or without potassium nitrate, and molten potassium hydrosulphate have no marked action on the alloy. F. Doerinckel found that the alloys resist cold aqua regia very well; soln. of potassium cyanide rapidly attack alloys with a low proportion of platinum; the action is slower with increasing proportions of platinum; and when 60 per cent. of platinum is present, the attack is slow with boiling soln. A.G. Norddeutsche Affinerie found that the alloys dissolve anodically in hydrochloroauric acid; and F. Haber found that 11 per cent. hydrochloric acid, at the b.p., attacks platinum anodes as vigorously as a 36 per cent. soln. at ordinary temp.; but an 8 per cent. soln., at the b.p., leaves the platinum intact, and a soln. below 30 per cent. hydrochloric acid does not attack the metal at ordinary temp. L. Quennessen studied the attack by caustic alkalies. P. Nicolardot and J. Boudet found that crucibles made with gold alloyed with 12·5 to 25 per cent. of platinum are badly attacked during the electrolysis of alkaline soln., and in the presence of sulphides, and sodium cyanide.

E. Jänecke represented the ternary **platinum-gold-copper alloys** as a continuous series of solid soln.; and the **platinum-gold-silver alloys** as a series of solid soln. with a gap, Fig. 51. E. Matthey noted the segregation of

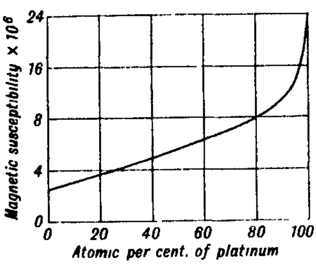


FIG. 50.—The Magnetic Susceptibility of the Platinum-Gold Alloys.

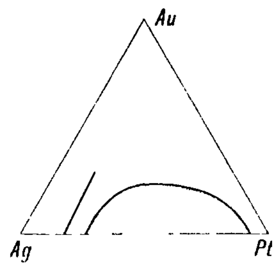


FIG. 51.—The Ternary System: Pt–Au–Ag.

both series of alloys. E. B. Craft and J. W. Harris said that the alloy with 67·5 to 70 per cent. of gold, 25 per cent. of silver, and 5 to 7·5 per cent. of platinum, is harder than platinum; and F. A. Bolley used the alloy 8 parts of platinum, 1 part of silver, and 3 parts of gold for dental work. L. N. Vauquelin, and H. Debray noted that nitric acid completely dissolves the alloy with 1 part of platinum, 10 parts of gold, and 30 parts or more of silver. A. von der Ropp noted that nitric acid dissolves most of the silver and gold, but leaves some platinum alloy undissolved; press. increased the solubility of the platinum. E. Matthey noted that castings of the quaternary **platinum-gold-silver-copper alloys** are not homogeneous. R. B. Graf used the 45 : 15 : 25 : 15-alloy for electric contacts. L. Nowack studied the **platinium-gold-zinc alloys.** N. H. Furman studied an application of the amalgam—**gold-platinum-mercury alloy**—in electrometric titrations.

According to M. Tarugi,[5] when platinum salts are heated with calcium carbide, a **platinum-calcium alloy** is formed, and it is easily decomposed by water. F. E. Carter said that when the platinum is melted under reducing conditions in a lime-crucible, it takes up calcium to form an alloy. E. D. Clarke observed that a **platinum-barium alloy** is formed by melting a mixture of the two elements in the oxyhydrogen flame. The bronze-coloured alloy disintegrates to a reddish powder in 24 hrs. A. Matthiessen found that in the electrolysis of molten barium chloride with a platinum cathode, a yellow, brittle alloy is formed, and it is slowly

decomposed by water with the separation of pulverulent platinum. H. Boving obtained surface films of alloys with alkaline earth metals by heating platinum wires in the vapour of the metal. The product was tried as a lamp filament.

According to W. R. E. Hodgkinson and co-workers,[6] the preparation of **platinum-magnesium alloys** is difficult because the vapour of magnesium is almost completely absorbed by the glass or porcelain containing vessel. If magnesium is heated with platinum in hydrogen, for some hours, a friable alloy corresponding with *platinum dimagneside*, $PtMg_2$, is formed. F. E. Carter said that platinum may take up magnesium to the extent of 3 per cent. M. Balbo noted the reduction of nitrobenzene to aniline by platinized magnesium ; and H. Princass, the spectrum of the Pt-Mg catalyst.

According to A. F. Gehlen,[7] and R. W. Fox, 1 part of spongy platinum unites with 1·5 to 2 parts of zinc, at a temp. below redness, producing a vivid combustion amounting to an explosion. R. Böttger, and J. Murray also noted the vigour of the reaction in the formation of **platinum-zinc alloys.** H. St. C. Deville and H. Debray observed that platinum dissolves in molten zinc, and alloys were made by C. Barus, C. Winkler, and C. T. Heycock and F. H. Neville by fusing a mixture of the two elements ; W. R. E. Hodgkinson and co-workers, and A. Pospieloff, by the action of the vapour of zinc on platinum ; F. Mylius and O. Fromm, C. A. Kohn and J. Woodgate, T. S. Price, and V. Engelhardt, by the electrodeposition of zinc on platinum ; J. W. Döbereiner, by the action of platinum on zinc-sodium alloys ; and F. Mylius and O. Fromm, by the action of zinc on soln. of platinum salts.

Some compounds have been reported, but the evidence in support of their chemical individuality is equivocal—*e.g.* W. R. E. Hodgkinson and co-workers reported crystalline **platinum zincide,** PtZn to be formed by strongly heating **platinum dizincide,** $PtZn_2$, which is said to be formed by heating platinum for 5 hrs. in the vapour of zinc. H. St. C. Deville and H. Debray obtained the dizincide by treating a platinum-zinc alloy, containing an excess of zinc, with hydrochloric acid, and H. Behrens, by treating the alloy with dil. sulphuric acid. H. Behrens said that the crystalline powder consists of brownish crystals—probably hexagonal. C. T. Heycock and F. H. Neville observed that molten zinc dissolves 4 per cent. of platinum without altering appreciably its f.p., and they obtained a product corresponding with **platinum hemitrizincide,** Pt_2Zn_3, with a m.p. which W. Guertler supposed corresponds with a eutectic temp. A. Westgren, U. Dehlinger, and W. E. Schmid studied the X-radiograms of the Pt_5Zn_{21}-alloy.

A. F. Gehlen, and R. W. Fox said that the alloys are bluish-white. H. Behrens observed that polished surfaces of alloys with 10 per cent. platinum, etched with dil. sulphuric acid, show the presence of rod- and needle-like crystals. A. J. Bradley discussed the X-radiograms. A. F. Gehlen, and R. W. Fox observed that platinum is rendered brittle when alloyed with 0·25 part of zinc, and zinc is rendered brittle by alloying with 0·05 part of platinum. C. Winkler also found that alloys with 90 to 99 per cent. of zinc are very brittle. C. Barus measured the electrical resistance, and its temp. coeff. R. W. Fox observed that the platinum-zinc alloys lose the greater part of their zinc by oxidation when they are heated in air. G. Tammann and W. Wiederholt studied the polarization of the alloy.

J. B. J. D. Boussingault found that the black powder which remains when an alloy with 80 per cent. of zinc is treated with dil. sulphuric acid contains 31 per cent. of zinc. These residues were also studied by H. Debray, and H. St. C. Deville and H. Debray—*vide supra*, explosive or fulminating platinum. A. von der Ropp observed that when the alloys are treated with nitric acid, a part of the platinum passes into soln. with the zinc. C. Winkler found that with alloys containing [Zn] per cent. of zinc, [Pt] per cent. of platinum passes into soln., thus :

Sp. gr. HNO_3	1·398		1·298		1·190		1·298 (fuming)		
[Zn]	90·00	98·71	90·46	98·87	98·84	98·83	90·79	96·74	per cent.
[Pt]	10·29	19·67	10·70	31·66	19·40	37·14	4·86	10·76	„

T. Cooper prepared a **platinum-copper-zinc alloy** by melting a mixture of the first two metals covered with borax and carbon in a crucible at a white-heat, and stirring in the zinc when the crucible had been taken from the furnace. The gold-coloured alloy does not rust, and it is attacked only by boiling nitric acid. J. J. Burle, and C. Krug also prepared these alloys. J. J. Burle also prepared **platinum-copper-silver-zinc alloy.** L. Nowack studied the age hardening of the **platinum-gold-zinc alloys.** F. Stromeyer prepared a **platinum-cadmium alloy** by heating platinum with an excess of cadmium until the excess is volatilized. A. Pospieloff, and W. R. E. Hodgkinson and co-workers also obtained an alloy by the action of the vapour of cadmium on platinum ; and F. Mylius and O. Fromm, by the precipitation of platinum by cadmium from soln. of platinum salts. K. W. Ray studied the equilibrium diagram.

F. Stromeyer, and W. R. E. Hodgkinson and co-workers' products corresponded with **platinum dicadmide,** $PtCd_2$. The silver-white, fine-grained product is very brittle. Its sp. gr. is 13·53 at 15°—calculated 12·59. Scarcely any cadmium volatilizes from the alloy at a red-heat. When digested with nitric acid, some platinum passes into soln. along with the cadmium. All the alloys with over 6 per cent. of platinum were found by K. W. Ray to be very brittle, and harder than either metal component. The cadmium is dissolved out by hydrochloric or sulphuric acid, leaving spongy platinum behind.

B. Wood noted the brittleness of these alloys. C. T. Heycock and F. H. Neville observed that the f.p. of cadmium is lowered about 4·5° by the addition of 1 at. per cent. of platinum. K. W. Ray found that platinum dissolves in molten cadmium, forming white alloys having a low m.p. The f.p. curve shows that platinum dicadmide, $PtCd_2$, and **platinum hemienneacadmide,** Pt_2Cd_9, are formed. The hemienneacadmide decomposes at 615° into cadmium and the dicadmide, which melts at 725°. The eutectic with 2 per cent. of cadmium and the hemienneacarbide melts at 315°. Cadmium volatilizes rapidly during the preparation of alloys with over 50 per cent. of platinum, and the pasty mass can be melted only under press. C. Barus made some measurements of the electrical resistance, and of its temp. coeff. G. Tammann and W. Wiederholt studied the polarization of the alloy. F. Mylius and O. Fromm found that hydrogen is given off turbulently when the alloy is treated with hydrochloric acid.

J. F. Daniell,[8] R. Böttger, E. Melly, I. N. Plaksin and S. M. Schtamova, and C. Engler and L. Wöhler prepared **platinum-mercury alloys,** or **platinum amalgams** by triturating spongy platinum with mercury. R. Böttger used a warm mortar, and J. F. Daniell found that the amalgamation is facilitated if water acidified with acetic acid is also present. C. Engler and L. Wöhler observed that owing to occluded oxygen, and oxidation films, platinum black amalgamates with difficulty; and M. Tarugi, that the grey mercury which separates when magnesium is added to a soln. of mercury salt, does not amalgamate platinum black by trituration. A. Tribe observed that platinum black which has been treated with hydrogen readily amalgamates with mercury in a few hours. T. Ihmori showed that platinum black absorbs mercury vapour; and C. Hockin and H. A. Taylor, that platinum rapidly amalgamates with mercury boiling in an evacuated vessel.

J. F. Daniell observed that compact platinum does not take up mercury at ordinary temp. even when kept in contact with it for 6 years, but if the mercury be heated—to 200°, according to F. E. Carter—the metal acquires a film of mercury which can easily be wiped off ; and J. M. Crafts added that a small proportion of mercury is taken up by the metal. E. N. Horsford also noted that compact platinum does not take up mercury at ordinary temp. M. Krouchkoll emphasized that for amalgamation, the surface of the compact metal should be thoroughly cleaned, and he recommended dipping the platinum in boiling nitric acid, and heating it to redness many times. W. Skey showed that the contact of platinum with aq. ammonia or alkali-lye prevents amalgamation by oxidizing the surface of the metal, but the metal amalgamates if in contact with mineral acids. G. McP. Smith

and H. C. Bennett said that amalgams, not mercury, alone "wet" the surface of platinum in consequence of their surface tension. E. Englisch observed that mercury attacks platinum at 400°; and C. Hockin and H. A. Taylor, that an amalgam is formed when red-hot platinum is plunged into mercury. F. E. Carter said that sodium amalgam attacks platinum, and there is a process for removing platinum from its crushed ore which is based on this reaction.

P. Casamajor observed that the union of platinum with mercury is favoured by contact with zinc; and J. S. C. Schweigger, that the amalgamation is hastened by galvanic action. R. Abegg and H. S. Hatfield, V. Borelli, W. L. Hardin, and T. Wilm noted the formation of amalgams when platinum is electrodeposited on a mercury cathode. W. W. Mather obtained the amalgam by heating platinic chloroiodide with mercury in a sealed tube. According to J. Schumann, and W. Kettembeil, platinum is best amalgamated by contact with alkali amalgams. A. C. Christomanos used ammonium amalgam. J. P. Joule, M. Tarugi, and O. Loew obtained amalgams by allowing mercury to stand in contact with hydrochloroplatinic acid for a long time; F. Mylius and O. Fromm, and A. Hilgar and E. von Raumer, by the action of mercury on soln. of platinum salts; R. Böttger, and M. Tarugi, by the action of sodium amalgam on ammonium chloroplatinate, and, according to C. Hockin and H. A. Taylor, on other platinum salts; H. St. C. Deville and H. Debray, by the action on platinum of a soln. of mercuric cyanide mixed with a little potassium cyanide; G. McP. Smith, by the action of platinum on a conc. soln. of potassium mercuric cyanide; and M. Tarugi, by reducing a mixed soln. of platinic and mercuric chlorides with magnesium, or hydrazine.

C. Paal and E. C. Auerswald, and E. C. Auerswald prepared *colloidal platinum amalgam* by using sodium protalbinate or lysalbinate as protective colloids, when mercury acts on a platinum hydrosol, by the reduction of a mixture of platinum hydrosol and mercuric oxide hydrosol, by reducing a mixed soln. of hydrochloroplatinic acid and mercuric chloride, and by mixing colloidal soln. of mercury and platinum. The catalytic action of the colloid on hydrogen dioxide, and electrolytic gas; and also the oxidation of carbon monoxide; and the reduction of nitrobenzene, have been studied.

The amalgam may appear as a viscid mass, which when heated boils up, loses its mercury, and leaves behind a finely-divided, black powder, or a grey, coherent mass of mercury. If pressure is applied during the ignition, A. von Mussin-Puschkin said that the product is fit for working into malleable platinum. E. Melly, and W. W. Mather observed that when pressed in chamois leather, or between the fingers, some mercury is exuded. J. Schumann obtained an amalgam of sp. gr. 10·386, containing 7·9 per cent. of platinum; and J. P. Joule obtained products with 12 to 43·2 parts of platinum to 100 parts of mercury. According to R. Böttger, the dull black powder obtained by heating the amalgam over a spirit lamp still retains $\frac{1}{13}$th of its weight of mercury. Boiling the residue with conc. nitric acid for 24 hours extracts only a trace of mercury, and the washed and dried residue has a vigorous catalytic action on hydrogen gas and alcohol. If the amalgam be heated to a higher temp., all the mercury is expelled, and grey, coherent platinum remains which no longer inflames a jet of hydrogen. If, instead of heating the platinum amalgam, it is digested with nitric acid, frequently renewed, the black powder which remains is mixed with a few shining particles of platinum. It does not ignite a mixture of hydrogen and air at ordinary temp., but does so if heated.

C. H. Latham studied the adsorption of water vapour by platinum amalgam. According to R. Sabine, if a drop of dil. sulphuric, hydrochloric, oxalic, or acetic acid be placed on the clean surface of a rich amalgam of a metal positive to mercury —*e.g.* copper, zinc, antimony, tin, or lead—the drop does not remain still as it would do on purified mercury, but sets itself into an irregular jerky motion; but with the amalgam of a metal negative to mercury—*e.g.* silver, gold, or platinum—the drop of acid remains quite still. The movement is attributed to alternate oxidation

of a portion of the surface of the amalgam by air outside the drop, and deoxidation by electrolysis in the interior of the drop. G. A. Hulett calculated that mercury which distils from an amalgam saturated with platinum at 200° contains 1 part of platinum in a hundred million parts of mercury. By distilling 6·70 grms. of mercury at 200° and 25 mm. press., the mercury would occupy 39,540 litres, and the 0·067 mgrm. of platinum in this vol. would show a partial press. of $0{\cdot}0_6 26$ mm., if platinum be monatomic in the state of vapour. This datum represents the vap. press. of platinum at 200°; and it follows that each c.c. of space or gas in equilibrium with platinum at 200°, contains $5{\cdot}3 \times 10^9$ atoms of platinum. C. Hockin and H. A. Taylor found that the e.m.f. of platinum amalgam against amalgamated zinc in dil. sulphuric acid, is 1·363 to 1·169 volt for liquid amalgam, 1·168 volt for solid amalgam, and 1·086 for amalgam with only a trace of platinum. Hydrogen is absorbed by even dilute amalgams, and G. Meyer studied the cathodic polarization of the amalgam.

According to H. Moissan, when platinum amalgam is shaken with water for 15 seconds or less, it forms an emulsion of a buttery consistency and having five times the vol. of the original amalgam. The product is stable and not affected by being heated to 100° or cooled to —80°. A section made at the latter temp. reveals small drops of water disseminated throughout the amalgam, giving the latter a cellular appearance. When exposed in a vacuum, it diminishes in vol., a little water and a small quantity of gas separating. The emulsion is also produced by shaking 2 c.c. of pure mercury with 12 c.c. of water to which some drops of a 10 per cent. platinic chloride soln. have been added, and when platinum amalgam is shaken with water, similarly treated, the increase in vol. is greater than with pure water. Platinum amalgam emulsifies similarly when shaken with sulphuric acid, aqueous ammonia, aq. or ammoniacal ammonium chloride soln., sodium chloride soln., glycerol, acetone, anhydrous alcohol, ether, oil of turpentine, carbon tetrachloride, or chloroform, and forms stable emulsions. Benzene is inactive. Platinum amalgam, to which sodium has been added, also increases in volume and emulsifies when shaken with water. P. Lebeau added that the property of forming emulsions is not exhibited by the other metals of the platinum group, and with platinum amalgam, the property is shown when only 0·038 per cent. of platinum is present. The platinum amalgam loses its property by admixture with amalgams of zinc, calcium, lead, or tin. The volume of the mass formed is dependent not only on the nature of the liquid, but also on the state of the platinum from which the amalgam was made, being much greater when the latter is finely-divided, although even in this case the effect is diminished if the metal be strongly heated before the amalgam is made. Microscopic examination of sections cut from the mass, obtained by shaking platinum amalgam with a soln. of gelatin and then cooling to the f.p. of mercury, show that it had a structure similar to that of soap lather, so that it is probably due entirely to surface tension. G. Michaud observed that a trace of platinum in mercury prevents the formation of ammonium amalgam from sodium amalgam and a soln. of ammonium chloride. N. Tarugi found that conc. nitric acid dissolves so much the more platinum the greater the proportion of mercury. Thus, from a mixture containing 4·64 per cent. of platinum and 95·35 of mercury, nitric acid dissolves the whole of the platinum; as the percentage of platinum present increases, the proportion of the total amount dissolved by the acid diminishes, whilst the proportion of mercury dissolved decreases from 99 per cent. in a mixture of 91·11 parts of mercury and 8·88 of platinum to zero for a mixture of 17·02 per cent. of mercury with 82·97 of platinum. J. W. Smith studied the adsorption of water vapour and benzene vapour by amalgamated platinum. F. Glaser discussed the solubility of platinum amalgam in a soln. of potassium cyanide—*vide supra*. J. W. Mallet prepared **platinum-silver-mercury alloys** by the action of silver amalgam on platinum.

C. and A. Tissier[9] prepared **platinum-aluminium alloys.** O. Brunck observed that aluminium dissolves platinum very slowly; 1 part of platinum required 2 hrs.

to dissolve in 6 parts of aluminium at a red-heat. The ease with which aluminium oxidizes, makes it difficult to prepare alloys by fusing the two metals together, and in order to protect the aluminium from oxidation, during the preparation of the alloys, M. Chouriguine recommended dipping it in a soln. of lithium chloride, and drying it by heat before melting the metal in an electric furnace. M. Chouriguine's observations on the f.p. of the platinum-aluminium alloys are summarized in Fig. 52. A compound, **platinum trialuminide,** $PtAl_3$, is formed, and it appears imbedded in a matrix of aluminium in the form of violet-black octahedral dendrites. Alloys richer in platinum appeared to contain another compound, but this was not identified. O. Brunck observed that when an alloy of 1 part of platinum and 6 parts of aluminium is treated with 2 per cent. hydrochloric acid, there remains a bronze-coloured powder of sp. gr. 6·688, and with a composition corresponding with platinum tritadecaluminide, Pt_3Al_{10}.

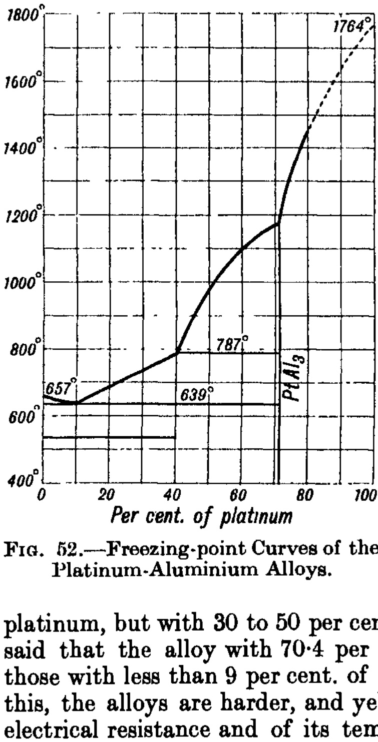


FIG. 52.—Freezing-point Curves of the Platinum-Aluminium Alloys.

According to M. Chouriguine, the white alloys with less than 10 per cent. of platinum are malleable, and take a good polish. The trialuminide is very hard, brittle, and easily powdered. Alloys with 70 to 80 per cent. of platinum are yellow, brittle, and fragile, and when digested with hydrochloric acid, they furnish a bronze-coloured crystalline powder; alloys with 80 to 90 per cent. of platinum are malleable, and resist acids. According to W. Campbell and J. A. Mathews, the introduction of up to 10 per cent. of aluminium does not perceptibly change the colour of platinum, but with 30 to 50 per cent., the alloys have a yellow tinge. F. E. Carter said that the alloy with 70·4 per cent. of aluminium, Al_3Pt, is hard and brittle; those with less than 9 per cent. of platinum are soft, malleable, and white; above this, the alloys are harder, and yellow. C. Barus made some observations on the electrical resistance and of its temp. coeff. K. Hélouis did not detect any change with the introduction of a small proportion of platinum. J. H. Gladstone and A. Tribe observed that aluminium with a layer of platinum decomposes water at 100°. A. Gawalowsky obtained a **platinum-gold-aluminium alloy,** a **platinum-gold-silver-aluminium alloy,** and the **platinum-silver aluminium alloy** known in commerce as *platalargan.*

A. Thiel [10] obtained a **platinum-indium alloy** by depositing indium on a platinum cathode. W. Crookes prepared **platinum-thallium alloys** by direct fusion; L. Hackspill, by dissolving platinum sponge in molten thallium; and F. Kuhlmann, by calcining thallous chloroplatinate. C. T. Heycock and F. H. Neville noted the effect of platinum on the f.p. of thallium. The alloys were studied by E. Zintl and A. Harder. The solubility of platinum in thallium or of thallium in platinum is very small. The only compound observed was **platinum thallide,** PtTl, which forms hexagonal crystals with a=5·605 A., and c=4·639 A. According to L. Hackspill, the m.p. of an alloy of platinum in thallium does not exceed that of thallium until the proportion of platinum attains 10 per cent., and as the proportion reaches 48·8 per cent., the m.p. rises to 685°. With increasing proportions of platinum, the m.p. at first falls slightly, but then rises continuously up to 855° for 65 per cent. of platinum. The m.p. goes on rising as more platinum is added. The maximum at 685° corresponds with the m.p. of **platinum thallide,** PtTl. Alloys rich in thallium contain brilliant white crystals

which are easily polished, and they are surrounded by a dark soft eutectic. When 48·8 per cent. of platinum is present, these crystals constitute the entire alloy. Alloys richer in platinum are susceptible of a high polish, their surface appears homogeneous, but their composite character is shown by oxidation in a bunsen flame. Platinum thallide forms steel-grey, prismatic needles, and it is obtained by the slow action of 10 per cent. nitric acid on alloys with less than 10 per cent. of platinum. It has a sp. gr. 15·65 at 14°, its hardness is 3 on Mohs' scale; and its sp. ht. is 0·0450. It loses a little thallium on continued heating above the m.p., but does not give pure platinum even on prolonged fusion in the oxyhydrogen flame. The alloy is attacked by the halogens, and dissolved by warm aqua regia; the latter on boiling, however, gives the insoluble thallium chloroplatinate. It is not attacked by hydrochloric acid, and only superficially acted on by sulphuric and nitric acids and by potassium hydrosulphate. It resists the action of the fused alkali carbonates, and is only very slowly attacked by sodium dioxide. It dissolves easily in fused zinc, lead, or silver. Its quantitative analysis, rendered very difficult by its properties, was effected by cupellation with four times its weight of silver and three times its weight of lead. The compound PtTl is very similar, especially in its physical properties, to the alloy PtPb. L. Hackspill prepared a **platinum-thallium-silver alloy** by dissolving silver in the platinum-thallium alloy; and a **platinum-thallium-zinc alloy** by dissolving zinc in the platinum-thallium alloy. Mercury below its b.p. forms a **platinum-thallium-mercury alloy,** or a **platinum-thallium amalgam.**

C. Winkler[11] observed that **platinum germanium alloys** can be readily obtained by adding platinum to molten germanium. According to H. Kellermann, platinum dissolves in molten cerium at about 800°. Much heat is developed during the formation of the **platinum-cerium alloys.** An alloy with 25 per cent. of platinum is hard and brittle, and it makes a good pyrophoric metal. The alloys were also examined by A. Hirsch.

A. F. Gehlen[12] prepared a **platinum-tin alloy** by heating together a mixture of spongy platinum with twice its weight of tin filings; and E. D. Clarke, and J. Murray noted that when tinfoil is rolled up with fine platinum foil, and heated before the blowpipe flame, combination occurs attended by a kind of explosion. H. Goldschmidt observed that the metals alloy below the m.p.; and H. Debray, and F. Doerinckel prepared alloys by melting mixtures of the two metals. An alloy was obtained by B. Delachanal and S. Mermet by reducing platinum purple of Cassius by hydrogen at a red-heat; by M. Faraday, by the electrolysis of molten stannous chloride with a platinum cathode; and N. W. Fischer, and F. Mylius and O. Fromm, by the precipitation of platinum with tin from a soln. of a platinum salt.

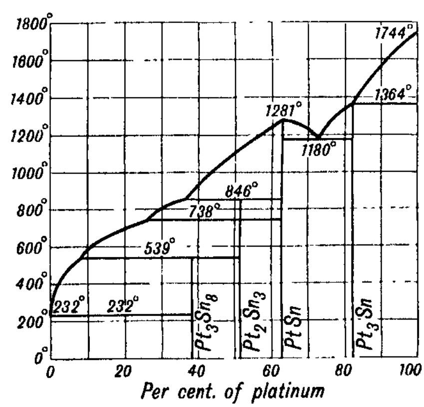


FIG. 53.—The Freezing-point Curves of the Platinum-Tin System.

F. Doerinckel, K. Honda and T. Ishigaki, and N. Podkopajeff studied the thermal equilibra in the binary system, and the results are summarized in Fig. 53. The f.p. curve of this system shows a eutectic at 1180°, four breaks, and a maximum at 1281°, and 62·5 per cent. of platinum, corresponding with **platinum stannide,** PtSn. This compound appears in hexagonal crystals, and is very brittle. I. Oftedal gave for the lattice dimensions a=4·103 A., c=5·428 A., and $a:c$=1:1·323. Whilst F. Doerinckel gave 1281° for the m.p., N. Podkopajeff gave 1324°. According to F. Doerinckel, the components of the eutectic at 1181° are platinum stannide and **platinum tritastannide,** Pt_3Sn;

this compound is stable only below 1364°, decomposing at that temp. into crystals of platinum, and a fused mass containing about 80 per cent. of that metal. M. Podkopajeff gave 1266° for the m.p. of this compound. According to F. Doerinckel, the break in the curve at 846° represents the interaction of platinum stannide and the fused alloy to form what is probably **platinum hemitristannide,** Pt_2Sn_3. H. St. C. Deville and H. Debray obtained this same compound by slowly cooling an alloy of platinum with six times its weight of tin, and then treating the product with hydrochloric acid; and P. Schützenberger, by the action of hydrogen on $Pt_2Sn_3O_2(OH)_2$, or on $Pt_2(SnO)_2SnO_2$. The greyish-white powder contains cubic or rhombohedral crystals. F. Doerinckel said that it exists in two allotropic forms, one stable below 738°, and the other stable between 738° and 846°. P. Schützenberger observed that when oxidized in air, it forms $Pt_2(SnO)_3$; and when heated in chlorine, stannous chloride distils off. F. Doerinckel observed that the f.p. curve at 538° has a break corresponding with a reaction between the hemitristannide and the fused alloy, to form what is probably **platinum tritaoctostannide,** Pt_3Sn_8. The compound forms long needles, and it decomposes when melted. The diagram was discussed by W. Guertler, and K. Bornemann.

Three other compounds have been reported although the f.p. curve does not indicate their existence. M. Lévy and L. Bourgeois observed that when $PtO_2.4SnO_2$ is reduced by hydrogen at a red-heat, and the product is treated with hydrochloric acid, **platinum tetritatristannide,** Pt_4Sn_3, is formed in lustrous plates with a black reflex. J. W. Mallet reported **platinum distannide,** $PtSn_2$, or Pt_4Sn_7, to be formed as a hard brittle mass which is easily pulverized. The sp. gr. is 10·72. Mercury amalgamated with a little sodium attacks this product. If an alloy with 2 per cent. of platinum is treated with very dil. hydrochloric acid, lustrous plates appear on the surface, and these are easily detached by a glass rod. A more conc. acid, or the application of heat, destroys the crystals. The analysis corresponds with **platinum tetrastannide,** $PtSn_4$. N. Podkopajeff also prepared this compound. With sodium chloride and chlorine at a red-heat, there is formed sodium chloroplatinate, and volatile stannous chloride; and at a red-heat, hydrogen chloride removes all the tin as stannous chloride. G. Tammann studied the subject.

A. F. Gehlen said that the alloy is tin-white, brittle, and with a laminated texture. F. Doerinckel observed that alloys with up to 20 per cent. of platinum are coarsely crystalline, and tin-white; alloys with 30 per cent. of platinum have a finer structure and are pale grey; alloys with between 40 and 55 per cent. of platinum have a fine crystalline structure, and are somewhat darker in colour; alloys with about 62·5 per cent. of platinum have a more lustrous fracture with with the same texture and colour; and with more platinum, the lustre decreases, and the colour becomes darker. According to F. M. Jäger and J. A. Bottema, the crystals of the monostannide, PtSn, are hexagonal with the same type of structure as NiAs, and the lattice has two mols. of PtSn per cell. The lattice parameters are a=4·103 A., and c=5·428 A. The calculated sp. gr. is 13·9. W. Lewis gave for the sp. gr. of the tin-platinum alloys:

Tin . .	50·4	66·3	80·0	88·9	92·3	96	100 per cent.
Sp. gr. .	10·827	8·972	7·794	7·705	7·613	7·471	7·180

F. Doerinckel found that the alloys with up to 30 per cent. of platinum are scarcely harder than their components, but beyond this point, the hardness rapidly increases, and attains a maximum with 80 per cent. of platinum. G. Wertheim found that an alloy with the proportions Sn : Pt=50·1, has a sp. gr. 7·578; an elasticity coeff. of 5309 kgrms. per sq. mm., a tensile strength of 4·75 kgrms. per sq. mm.; and the velocity of sound 7·890 (air unity). F. M. Jäger and J. A. Bottema gave 1281° to 1330° for the limits of the m.p.; this estimate is based on F. Doerinckel's 1281°; and N. Podkopajeff's, 1330°. The heat capacity, Q cals., between θ and 0° is:

θ . .	189·74°	221·88°	418·67°	644·90°	718·30°	802·06°	1044·80°
Q . .	7·3728	8·6419	16·5282	25·8917	28·9991	32·5927	43·4606

or $Q=0.038366\theta+0.0_5253626\theta^2+0.0_9359597\theta^3$; for the sp. ht. $c_p=0.03836+0.0_5507244\theta+0.0_8107879\theta^2$; and for the mol. ht., $C_p=12.0422+0.00159244\theta+0.0_633866\theta^2$. The data for the mol. ht. do not follow Neumann's rule—**1.** 13, 13. An alloy with the at. proportions Sn : Pt=1 : 0·1, was found by A. Matthiessen to have at 21° an electrical conductivity of 9·37 (silver 100); and C. Barus made observations on the electrical resistance and its temp. coeff. C. Hockin and H. A. Taylor found the e.m.f. of an alloy against amalgamated zinc, in dil. sulphuric acid, to be 0·548 volt, and in a conc. soln. of zinc sulphate, 0·484 volt; the corresponding data for the amalgamated alloy are respectively, 0·552 and 0·409 volt. Low fusing alloys are formed when tin is melted in contact with platinum. G. Tammann and W. Wiederholt studied the polarization of the alloy.

F. Doerinckel found that dil. hydrochloric acid readily attacks alloys with 0 to 30 per cent. of platinum, and with increasing proportions of platinum, the attack becomes slower, so that an alloy with 40 per cent. of platinum is attacked very slowly by the conc. acid. As indicated above, H. St. C. Deville and H. Debray obtained platinum hemitristannide as a residue after treating the alloy with dil. hydrochloric acid. P. Schützenberger noted that some black scales resembling graphite may be formed as a residue after treatment with hydrochloric acid. H. Debray said that the residues form black scales which resemble graphite, and contain in addition to the platinum metal a considerable proportion of tin, together with small quantities of oxygen and hydrogen. Their composition, however, is very variable. They behave like platinum-black, developing more or less heat when placed in an atm. of hydrogen, and causing the detonation of explosive gaseous mixtures. The development of heat is not merely a result of the condensation of the hydrogen in the pores of the substance, but is partly due to the reduction of some oxidized metal, and the consequent formation of water. Probably many substances which are called platinum-black are of a similar nature, and act in a similar manner. When the metallic residues are heated in vacuo they lose water, and afterwards deflagrate without losing oxygen, and sometimes even become incandescent. They are more readily attacked by reagents than the metals which they contain. F. Doerinckel found that alloys with up to 80 per cent. of platinum are readily attacked by aqua regia, and the attack is slower as the proportion of platinum increases; alloys with 90 per cent. of platinum are attacked with difficulty by aqua regia, and by chlorine. J. W. Mallet obtained a **platinum-tin-mercury alloy,** or **platinum-tin amalgam,** by the action of mercury on the platinum-tin alloy.

J. J. Berzelius[13] observed that when molten lead is poured into a platinum crucible, some of the platinum is dissolved; J. Murray found that when lead is wrapped in platinum foil and heated, union occurs with incandescence; C. Ridolfi, and A. F. Gehlen prepared **platinum-lead alloys** by heating to redness, 1 part of spongy platinum and 2·7 parts of lead—combination occurs without incandescence, and an easily fusible alloy is formed. Alloys were also made by C. Winkler, H. Goldschmidt, S. de Luca, A. Bauer, C. Barus, and F. Doerinckel by fusing together the constituent metals; C. A. Martius, by heating lead cyanoplatinite to a high temp.; and according to F. Mylius and O. Fromm, lead forms the alloy when it is used to precipitate platinum from platinum salt soln. C. T. Heycock and F. H. Neville found that 0·148, 0·299, and 0·600 at. per cent. of platinum in lead lowered the f.p. 6·42°, 6·5°, and 6·3° respectively. Observations on the f.p. of the binary system were made by W. Guertler, K Honda and T. Ishigaki, G. Tammann, and K. Bornemann. F. Doerinckel found that the f.p. curve, Fig. 54, contains these breaks and a eutectic so that none of the three components which these metals form is stable at their respective m.p. The compound richest in platinum could not be identified owing to the small thermal effect. It is stable below 910°. W. Guertler suggested that it may be **platinum tritaplumbide,** Pt_3Pb, analogous with the corresponding stannide, or it may be platinum tetritaplumbide, Pt_4Pb. F. Doerinckel found that this compound reacts with the fused mass at 787° to

form **platinum plumbide,** PtPb, which was also prepared by A. Bauer by fusing platinum with a small excess of lead, under borax, and dissolving out the excess of lead by acetic acid. N. A. Puschin and P. N. Laschtschenko observed that the compound, under the microscope, appears in six-rayed stars which always lie on crystals of the diplumbide. A. Baur said that the crystalline mass resembles bismuth, and has a reddish colour. It is very brittle, and has a sp. gr. 15·736 to 15·77. It is decomposed by boiling mineral acids, but not by dil. acetic acid. F. Doerinckel observed that the compound decomposes when melted, and when cooled, it reacts with the fused alloy at 385° to form a third compound which K. Bornemann suggested may be **platinum hemitriplumbide,** Pt_2Pb_3. The eutectic between this compound and lead contains 5 per cent. of platinum, and solidifies at about 290°. H. Senn reported **platinum diplumbide,** $PtPb_2$, to be obtained by electrolyzing an acidic soln. of lead fluosilicate with an alloy of lead with 10 per cent. of platinum as anode; the anode mud contains brilliant plates of the diplumbide which N. A. Puschin and P. N. Laschtschenko described as prismatic crystals. H. Senn added that if the current density exceeds 1 amp. per sq. dm., the compound decomposes. It is decomposed by nitric acid.

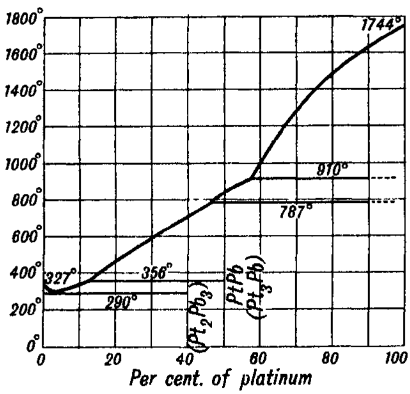


FIG. 54.—Freezing-point Curves of the Platinum-Lead System.

According to A. F. Gehlen, the alloy, with platinum and 2·7 times its weight of lead, has the colour of bismuth, splits under the hammer, and has a fibrous fracture; the 50 : 50-alloy has a purple colour, and striated surface, and it is hard and brittle, and exhibits a granular fracture. W. Lewis found the sp. gr. of some alloys to be:

Pb . .	49·2	65·8	80·0	88·9	92·3	96·0	100 per cent.
Sp. gr. .	14·029	12·925	12·404	11·947	11·774	11·575	11·386

F. Doerinckel said that the hardness of these alloys increases gradually as the proportion of platinum rises to 45 per cent.; with from 45 to 85 per cent. of platinum, the alloys are rather harder than fluorite. Alloys containing 5 to 30 per cent. of platinum are readily fractured by pressure. The fracture of alloys with 5 to 30 per cent. of platinum is very coarsely crystalline; with 40 to 50 per cent. of platinum, the fracture is less coarsely crystalline, and reddish; with 60 per cent. of platinum, the fracture and colour resemble hardened steel. G. Wertheim found the coeff. of elasticity for an alloy with the at. proportion Pb : Pt=85 : 1, and sp. gr. 11·473, is 2684 kgrms. per sq. mm., and with alloys 6 : 1 and sp. gr. 12·207, 3107·5 kgrms. per sq. mm.; the elastic limit of the 85 : 1 alloy is 0·4 to 0·6 kgrm. per sq. mm.; the tensile strength is 1·65 kgrms. per sq. mm. The velocity of sound with the 85 : 1-alloy is 4·560 (air unity), and with the 6 : 1-alloy, 4·756. A. Matthiessen found the electric conductivity of an alloy with the at. proportion Pb : Pt=1 : 0·1 to be 5·18 (silver 100) at 21·4°. C. Barus measured the electrical resistance and its temp. coeff. According to N. A. Puschin and P. N. Laschtschenko, the e.m.f. of the alloys against lead in N-$Pb(NO_3)_2$ soln. furnishes a curve with two breaks, corresponding respectively with platinum plumbide, and diplumbide. For alloys with up to 33 at. per cent. of lead, the e.m.f. is the same as for lead; there is then a sudden drop corresponding with $PtPb_2$; and there is a second fall with 50 at. per cent. of lead corresponding with PtPb. G. Tammann and W. Wiederholt studied the polarization of the alloy.

A. F. Gehlen observed that the exposed fracture of the 50 : 50-alloy is altered

by exposure to air ; and H. St. C. Deville found that the lead of alloys with only a small proportion of platinum slowly passes into carbonate. F. Doerinckel showed that the grey, freshly fractured surfaces of alloys with 5 to 30 per cent. of platinum oxidize rapidly on exposure to air ; the alloy with 2·5 per cent. of platinum oxidizes rapidly on exposure to air ; the alloy with 2·5 per cent. of platinum oxidizes more rapidly than lead ; air acts very slowly on alloys with 40 to 50 per cent. of platinum, and not at all on alloys with more platinum. A. F. Gehlen found that when the alloys are heated to redness in air, only part of the lead separates from the platinum ; and that the separation continues only so long as the alloy remains fusible ; the subject was studied by H. St. C. Deville and H. Debray. A. Bauer and P. von Mertens showed that sulphuric acid decomposes an alloy with 10 per cent. of platinum slowly and incompletely ; and an alloy with 2 per cent. of platinum suddenly and completely at 260° to 280°. According to A. von der Ropp, nitric acid attacks all alloys with up to 50 per cent. of lead rather rapidly, and the attack with alloys containing more platinum was found by F. Doerinckel to be slower. H. Senn discussed the residues, and H. Debray, the explosive residues —*vide* zinc. Some platinum passes into soln. along with the lead. C. Winkler found that with alloys containing [Pb] per cent. of lead, [Pt] per cent. of platinum passes into soln. :

Sp. gr. HNO_3 .	1·398		1·298		1·09	
[Pb] . .	90·20	98·60	90·46	98·64	88·75	98·88
[Pt] . .	7·19	21·33	9·09	17·80	8·33	22·50

L. Hackspill prepared a **platinum-thallium-lead alloy** by dissolving lead in the platinum-thallium alloy.

According to J. J. Berzelius,[14] a platinum crucible in which preparations of vanadium have been frequently ignited becomes covered with a thin film of a **platinum-vanadium alloy,** without altering its colour or lustre. When heated in air, a film of fused vanadic acid is formed which prevents the further oxidation of the alloyed vanadium.

R. Karlen [15] prepared some **platinum-tantalum alloys** in an electric furnace in vacuo. Alloys with 1 to 2 per cent. of tantalum can be rolled below redness. The addition of 1 per cent. of tantalum increases the hardness of platinum 25 to 30 per cent. ; and 2 per cent. of tantalum augments the hardness nearly 40 per cent. According to M. G. Korsunsky, solid soln. are formed. The alloys are not altered by air at a high temp., or by sulphuric, hydrochloric, nitric, or hydrofluoric acid, or by a conc. soln. of potash-lye. Fused potassium hydrosulphate has no action ; and fused sodium or potassium carbonate has only a very feeble action. The alloys are also attacked by aqua regia.

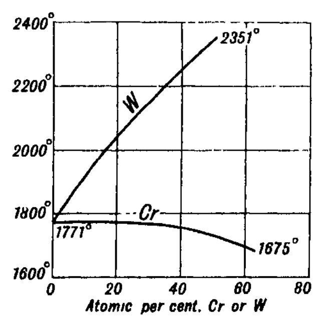


FIG. 55.—The Liquidus Curves of Alloys of Platinum with Chromium and Tungsten.

C. Barus [16] prepared **platinum-chromium alloys** by melting a mixture of the two metals in an oxy-hydrogen furnace. W. Guertler made some observations on these alloys. M. G. Korsunsky said that solid soln. are formed. C. Barus measured the electrical resistance of the alloys. L. Müller determined the liquidus curve of some platinum-chromium alloys, and the results are summarized in Fig. 55. V. A. Nemiloff studied the hardness, conductivity, etc., of the alloys, and observed evidence of the formation of **platinum hemichromide,** Pt_2Cr, and of **platinum chromide,** PtCr, but not on the thermal diagram, which shows only solid soln. E. Friederich and A. Kussmann detected a compound **platinum trichromide,** $PtCr_3$, in the alloy, and they studied the ferromagnetism of the alloys. Measurements of the electrical resistance were also made. E. Friederich found that the alloys with 2 to 15 per cent. of chromium

are magnetic with a maximum at 10 per cent. of chromium; the magnetic transition point is 390° to 400°. E. Jänecke discussed the ternary systems involving **platinum-chromium-copper alloys,** also the **platinum-chromium-silver alloys,** and the **platinum-chromium-gold alloys.**

C. Barus, C. F. Dreibholz, W. Guertler, and W. Lederer prepared some **platinum-molybdenum alloys** according to the method employed for the platinum-chromium alloys. M. G. Korsunsky said that solid soln. are formed. C. Barus measured the electrical resistance. P. J. Hjelm found that an alloy with 50 per cent. of molybdenum was pale grey, hard, and brittle, and an alloy with 20 per cent. of molybdenum was bluish-grey, hard, brittle, with a granular fracture. J. J. and F. de Elhuyar, and E. Haagn and W. C. Heraeus prepared **platinum-tungsten alloys** from the two metals; and E. Weintraub, by drawing thin wires of the two metals and melting them in the electric furnace. The alloys with 20 to 60 per cent. of platinum are malleable, and harder than platinum. M. G. Korsunsky said that solid soln. are formed. The alloy also resists oxidation when heated in air, and attack by chemical reagents better than platinum. L. Müller determined the liquidus curve of some platinum-tungsten alloys, and the results are summarized in Fig. 55. Measurements of the electrical resistance were also made. I. E. Adadaroff and co-workers studied the oxidation of ammonia using the platinum-tungsten-silver, and platinum-tungsten-rhodium alloys as catalysts. T. Meiffren prepared a **platinum-gold-copper-tungsten alloy.**

J. Aloy electrolyzed molten potassium chlorouranate, with platinum electrodes, and obtained a **platinum-uranium alloy.**

C. Barus [17] prepared **platinum-manganese alloys** by melting a mixture of the two elements in the oxyhydrogen flame. He studied the electrical resistance of some alloys. W. Guertler made some observations on these alloys.

E. Jänecke discussed the ternary systems involving **platinum-manganese-copper alloys,** and the **platinum-manganese-silver alloys.** W. Goedecke, F. Beck, and A. Schulze studied the thermoelectric force of platinum against a **platinum-rhenium alloy.**

H. St. C. Deville [18] reported native *ferroplatinum* associated with 13 per cent. of iron; A. Breithaupt, J. J. Berzelius, G. Osann, A. von Mussin-Puschkin, and H. Debray reported up to 19 per cent. of iron; and other observations have been made by A. Terreil, A. Daubrée, and H. St. C. Deville and H. Debray. J. Stodart and M. Faraday prepared some alloys, and some of their properties were examined by R. A. Hadfield, and H. List. E. D. Clarke found that **platinum-iron alloys** can be obtained by heating equal parts of the two metals in an oxyhydrogen flame; C. Barus employed a similar process; W. Lewis, and A. F. Gehlen said combination does not occur in an ordinary furnace, although H. St. C. Deville said that the metals unite at a comparatively low temp. E. Isaac and G. Tammann melted mixtures with up to 50 per cent. of platinum in a porcelain tube, and mixtures with 50 to 90 per cent. of platinum in a magnesia tube, and in an atm. of nitrogen. H. St. C. Deville and H. Debray obtained an alloy by heating platinum with 10 parts of pyrite, and 1 part of borax, and treated the product in turn with nitric acid, potash lye, and hydrofluoric acid. J. B. J. D. Boussingault dissolved equal parts of the two metals in aqua regia, removed the excess of acid by evaporation, added aq. ammonia, and heated the washed precipitate in a current of hydrogen at a low red-heat. The alloy was pyrophoric. F. Mylius and O. Fromm said that iron in dil. soln. of platinum salts forms an iron-platinum alloy. F. E. Carter discussed the contamination of platinum by contact with iron during annealing operations; and in rolling, and wire drawing iron may be embedded in the surface of platinum, and on subsequent heating, dissolved by the metal. Hence, before reheating, the adherent iron should be removed by hot, conc. hydrochloric acid. N. Agéeff and M. Zamotorin studied the diffusion of platinum in iron; and W. C. Roberts-Austen showed that at 492° 1·69 grms. diffuse per sq. cm. per day, or $1{\cdot}96 \times 10^{-5}$ grm. per second in iron. M. G. Korsunsky said that solid

soln. are formed. E. Isaac and G. Tammann observed that the two metals at a high temp. form a continuous series of solid soln., Fig. 56, but as the temp. falls, this decomposes into two other series of solid soln. extending from 0 to 50 per cent. platinum, and from 60 to 100 per cent. platinum. W. A. Nemiloff's values for the temp. coeff. of the resistance of the annealed and quenched alloys, and the singular points, have some analogies with the hardness curves. There are breaks in the cooling curves of alloys with 0 to 40 per cent. of platinum and with from 70 to 90 per cent. of platinum—owing to a modification in the crystals of the solid soln. rich in platinum. Alloys with up to 10 per cent. of platinum have two breaks corresponding with the transitions from γ- to β-iron, and from β- to α-iron, respectively. There is only the change from γ- to α-iron in alloys having 10 to 40 per cent. of platinum. All the alloys from 0 to 90 per cent. of platinum are magnetic, and this property appears to diminish in the same ratio as the iron, from 80 to 20 per cent. of that metal. The alloys from 10 to 50 per cent. of platinum lose their magnetic power on heating at temperatures varying from 800° to 650°, and this property returns on cooling at much lower temperatures; the curve of temperature at which the magnetic power reappears practically coincides with that representing the transformation γ- to α-iron referred to above. On the other hand, the temperatures at which the alloys containing 60 to 90 per cent. of platinum regain their magnetic power are much lower than the breaks in the cooling curve in this region. P. Oberhoffer, L. Graf and A. Kussmann, F. Wever, and W. Guertler also made observations on these alloys.

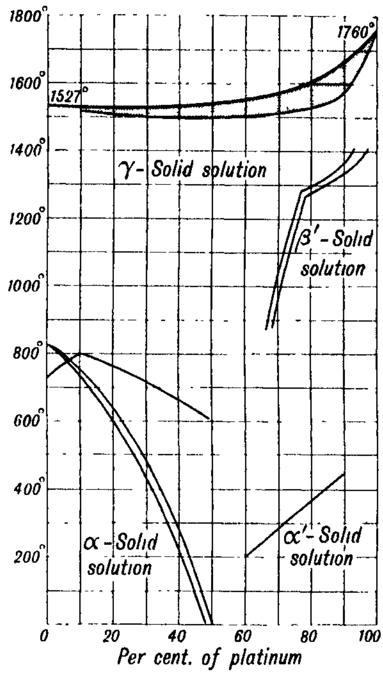


FIG. 56.—Freezing-point Curves of the Platinum-Iron Alloys.

According to E. Isaac and G. Tammann, the colour of the alloys becomes paler as the proportion of platinum increases. The structure of the alloys with about 88 per cent. of platinum is very similar to that of native ferroplatinum. G. H. Billings added that the fracture of alloys with 1 per cent. of platinum is not essentially different from that of iron, but the grain is rather finer, resembling more or less closely the fracture of a 0·3 per cent. carbon steel. W. A. Nemiloff discussed the microstructure of the alloys. The sp. gr. of an alloy with 0·82 per cent. of platinum, and 0·08 per cent. of carbon is 7·861. W. Lewis gave for the sp. gr. of the platinum-iron alloys:

Iron .	56·4	76·9	83·7	90·9	92·3	100 per cent.
Sp. gr. .	9·901	8·700	8·202	7·862	7·800	7·100

E. Isaac and G. Tammann said that the hardness of the alloys decreases with a proportion of platinum up to 5 per cent., and the hardness then gradually rises as the proportion of platinum increases up to 40 per cent. of platinum; beyond that point up to 90 per cent. platinum, the hardness remains constant. The brittleness of the alloys reaches a maximum at 50 per cent. platinum. W. A. Nemiloff observed Brinell's hardness for the annealed (A) and quenched (Q) alloys and obtained for alloys with:

Pt .		0	8·94	27·74	48·87	61·83	67·53	70·68	77·60	90·41	96·32% wt.
		0	2·71	9·89	21·42	31·67	37·30	40·82	49·78	72·95	88·22% at.
Brinell	A	67·79	118·48	148·34	197·84	203·38	251·39	268·56	161·68	110·64	65·69
	Q	70·39	100·81	146·65	137·78	—	109·62	118·01	147·08	94·94	59·28

The results are summarized in Fig. 57. In the quenched samples two solid. soln. are indicated with 0 to 40 at. per cent. of platinum, and 35 to 100 at. per cent. with the annealed samples, the first maximum corresponds with the formation of a **platinum ferride,** PtFe. G. H. Billings said that platinum makes iron harder, but less so than does the same proportion of carbon. E. Jänecke observed that the lowest m.p., 1500°, occurs with alloys having 7 at. per cent. of platinum. W. Wien

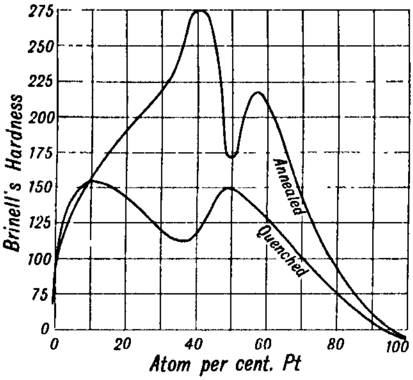


FIG. 57.—The Hardness of the Iron-Platinum Alloys.

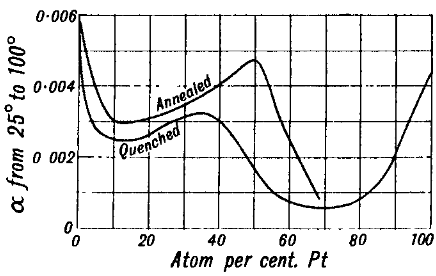


FIG. 58.—The Temperature Coefficient of the Electrical Resistance of the Fe-Pt Alloys.

studied the optical properties of an alloy of iron and platinum. C. Barus measured the electrical resistance and its temp. coeff. L. W. Haase studied the oxygen depolarization current; and J. Würschmidt, the thermoelectric force. H. St. C. Deville and H. Debray said that alloys with 17 and 20 per cent. of iron are magnetic. A. Daubrée found that an alloy with 16·87 per cent. of iron exhibits magnetic polarity, but an alloy with 11 per cent. of iron is only feebly magnetic. F. Aallot studied the Curie point, and the magnetic moment. W. Jellinghaus studied the coercive force.

C. F. Schönbein observed that an alloy with 1 per cent. of platinum is not attacked by nitric acid, and this was confirmed by P. Monnartz. The alloys are soluble in aqua regia. According to J. B. J. D. Boussingault, if the pyrophoric alloy, just mentioned, be placed in hydrochloric acid, without coming in contact with air, part of the iron dissolves with the evolution of hydrogen. The heavy, black powder which remains as a residue after washing contains about 20 per cent. of iron which may be dissolved out with nitric acid, and it also contains a trace of moisture but no hydrogen. The residue takes fire in air below a red-heat, and burns with the emission of sparks. Sometimes the combustion begins at the hottest part, and spreads throughout the mass with a red light, as in the burning of tinder. The powder, after combustion, gains 1 per cent. in weight.

J. Murray did not obtain alloys of platinum and steel at the temp. of an alcohol flame. W. Lewis said that platinum forms with cast iron a dark, malleable, very hard alloy; G. H. Billings prepared an alloy with 4 per cent. platinum with cast iron containing 2 per cent. of carbon, and found that it could be hammered and rolled though showing signs of red-shortness. J. Stodart and M. Faraday described the following platinum-steel alloys: 9 : 2-alloy: perfect alloy, sp. gr. 15·88, does not tarnish in air; 1 : 1-alloy: crystalline structure, sp. gr. 9·862, takes high polish, does not tarnish in air; 1 : 8-alloy: finely damasced alloy; 1 : 10-alloy: sp. gr. 8·1; 1 : 67-alloy: best adapted for cutting instruments; and 1 : 100-alloy: uniform surface, fine fracture, not so hard as silver-steel, but is much tougher. J. R. Bréant, and H. Bush found that the 1 : 200 alloy can be damasced very well and is adapted for razors. H. Remy and H. Gonnington studied the catalytic effect in the hydrogen-oxygen reaction. J. Stodart and M. Faraday found that steel

alloyed with a small proportion of platinum dissolves in dil. sulphuric acid more quickly than with steel without the platinum; the acceleration can be detected with 0·0025 part, and is most marked with 0·005 to 0·01 part; with 0·025 part, the solubility is perceptibly slower, and steel with 0·5 part does not dissolve more quickly than steel alone; an alloy of 2 parts of steel with 9 of platinum is not affected by dil. sulphuric acid. These alloys behave in an analogous way with other acids. When 100 parts of steel are alloyed with 1 part of platinum, or any other metal insoluble in nitric acid, and treated with dil. sulphuric acid, and the undissolved portion—containing iron, carbon, hydrogen, and platinum—is boiled with nitric acid, a black residue is left. This latter substance, when heated to 200°, detonates slightly, producing a faint light, but if gradually heated, decomposition occurs without detonation. It dissolves in aqua regia yielding a soln. containing a large proportion of platinum, and but little iron. Observations on the subject were made by H. Debray, and F. Osmond and J. Werth—*vide supra*, explosive platinum. H. Sawamura observed the effect of platinum on the graphitization of cast iron.

E. Maumené prepared a **platinum-iron-copper alloy** by melting a mixture of the component metals under borax. W. Goedecke studied some **platinum-iron-gold alloys.** E. Jänecke made some observations on the ternary system; and also on that of the **platinum-iron-silver alloys;** that of the **platinum-iron-chromium alloys;** and of the **platinum-iron-manganese alloys.**

C. Barus [19] prepared **platinum-cobalt alloys** by fusing a mixture of the two elements in the oxyhydrogen flame. W. Guertler studied the subject. According to M. G. Korsunsky, solid soln. are formed. C. Barus measured the sp. elastic resistance of some alloys. V. A. Nemiloff found that the platinum-cobalt system consists of an unbroken series of solid soln.—Fig. 62—with a minimum m.p. for 25 at. per cent. of platinum. Alloys of maximum Brinell's hardness, contain 11·6 and 50·6 at. per cent. of platinum—Fig. 63. The sp. electrical resistances of alloys with 97·54, 94·64, and 92·98 per cent. of platinum are, respectively, $R\times10^6$=31·27, 39·08, and 41·49 at 25°, and 34·39, 42·81, and 45·84 at 100°, so that the temp. coeff. are, respectively, 0·001375, 0·001314, and 0·001449. F. E. Carter said that the alloys have a higher electrical resistance than is the case with the nickel alloys. Alloys with 2·5, 5, and 10 per cent. of cobalt have the respective resistances 170, 245, and 155 ohms per million ft. The alloys are workable with up to 10 per cent. of cobalt. G. Grube and H. Kästner studied the conductivity of the alloys. L. Néerl, and F. W. Constant studied the magnetic properties of some alloys with 5 to 10 per cent. of cobalt. No evidence of a eutectic was observed, but many crystals show a cubic formation. The Curie points of alloys of cobalt with platinum and the maximum intensity of magnetization, $I_{max.}$, obtainable at the temp. of liquid air, −194°, were found by F. W. Constant to be:

Platinum	90	95	97	98·5 per cent.
Curie point	249°	49°	−82°	−191°
I_{max}	364	254	104	7

W. Jellinghaus measured the coercive force of the alloys. H. Remy and H. Gonnington studied the catalytic effect of the alloy in the hydrogen-oxygen reaction. E. Jänecke studied the ternary systems involving the **platinum-cobalt-copper alloys;** the **platinum-cobalt-silver alloys;** and the **platinum-cobalt-iron alloys.**

The association of nickel with native platinum was observed by A. Terreil,[20] and A. Daubrée. W. A. Lampadius prepared a **platinum-nickel alloy** by heating a mixture of equal parts of the two metals on charcoal burning in oxygen; and C. Barus melted the metals in the oxyhydrogen flame. L. Nowack discussed the so-called *white gold alloys*. The alloy with 5 per cent. of nickel is used as the heating filament in radio tubes. The alloys were studied by J. Cournot, W. Guertler, and L. Nowack. According to M. G. Korsunsky, solid soln. are formed. W. A. Lampa-

dius said that the pale yellowish-white alloy is quite malleable, takes a high polish, and is equal to copper in fusibility, and to nickel in magnetic power. N. S. Kurnakoff and V. A. Nemiloff observed no evidence of the formation of a chemical compound of nickel and platinum on the f.p. curve, Fig. 59. The alloys form two types of solid soln., one with less and the other with more than 20 at. per cent. of platinum. The Brinell's hardness curve is shown in Fig. 60—*vide* Table IV.; and the electric resistance and temp. coeff. between 25° and 100°, in Fig. 61. W. C. Heraeus found that by heating alloys with 8 to 15 per cent. of platinum to 800°, there is only a slight loss in tensile strength, and elasticity. C. Barus measured the sp. electric resistance and its temp. coeff. F. E. Carter said that a 10 per cent. alloy has a resistance of 180 ohms per million ft., and a 5 per cent. alloy, 140 ohms per million ft., and a temp. coeff. of 0·00189 per degree between 0° and 1200°. M. Hartmann and M. Braun, and J. Würschmidt measured the thermoelectric force; L. Néerl, C. Manders, F. W. Constant, the magnetic properties; and A. B. Jones, the photoelectric effect. K. Hélouis noted that the alloys resist oxidation when heated in air. H. Remy and H. Gonnington studied the catalytic effect in the hydrogen-oxygen reaction. G. Tammann's study of the action of gold chloride, nitric acid sp. gr. 1·44, fuming hydrochloric acid, soln. of copper chloride, ferric chloride, ammonium sulphide, and sodium polysulphide showed that the reactions are limited with alloys having up to 25 per cent. of platinum. A. Gawalowsky said that the nickel-platinum alloy, known in commerce as *platnik*,

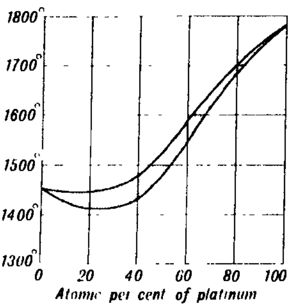


FIG. 59.—The Freezing-point Curves of the Ni-Pt Alloys.

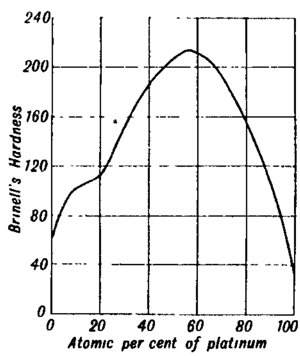


FIG. 60.—The Hardness of the Ni-Pt Alloys.

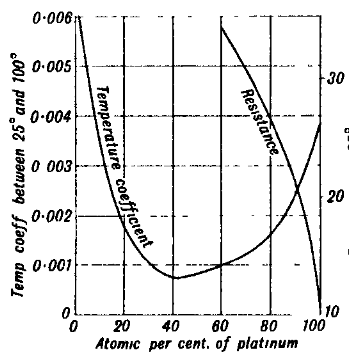


FIG. 61.—The Electrical Resistance and Temperature Coefficient of the Ni-Pt Alloys.

can be used as a substitute for platinum in analytical operations. E. Jänecke studied the ternary systems involving the **platinum-nickel-copper alloys**; and the **platinum-nickel-silver alloys.** W. and R. Borchers prepared a **platinum-nickel-silver-chromium alloy**; H. Bush, a **platinum-nickel-silver-tin alloy**; and W. and R. Borchers also prepared some more complex alloys. E. Jänecke studied the ternary system, involving the **platinum-nickel-gold alloys**; and the **platinum-nickel-iron alloys.** W. and R. Borchers described a **platinum-nickel-cobalt-chromium alloy,** and also a **platinum-nickel-cobalt-chromium-molybdenum alloy.**

According to F. E. Carter,[21] ruthenium hardens platinum to about the same extent as does osmium. The limit of workability is about 10 to 15 per cent. of ruthenium. The Brinell's hardness of the annealed alloy, with 10 per cent. of ruthenium, is 210—*vide* Table IV—and its electrical resistance, 245 ohms per million ft. L. Holborn and A. L. Day measured the thermoelectric force of a

platinum-ruthenium alloy, 90 : 10, against platinum, and found that with the cold joint at 0°, the thermoelectric force, E millivolts at :

	−185°	0°	200°	400°	600°	800°	1000°	1200°	1500°
E .	−0·53	0	1·59	3·58	5·74	8·01	10·41	12·90	16·58

F. E. Carter said that the alloys lose weight on heating owing to the volatilization of ruthenium, but not so much is lost as in the case of the alloy with osmium

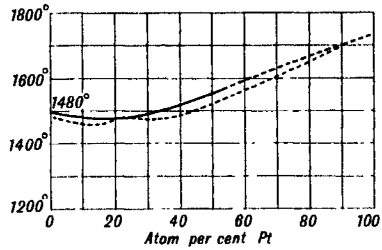


FIG. 62.—Freezing-point Curves of Co-Pt alloys.

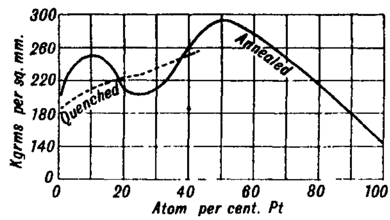


FIG. 63.—The Hardness of the Co-Pt alloys.

H. Remy and H. Gonnington studied the catalytic effect in the hydrogen-oxygen reaction. G. R. Levi found that the presence of 10 per cent. of ruthenium scarcely affected the catalytic activity of platinum on hydrogen dioxide ; D. Martienssen also used the alloy as a catalyst.

According to G. K. Burgess and P. D. Sale,[22] **platinum-rhodium alloys** are readily produced. R. B. Sosman observed that no compounds, but only solid soln. of the two elements, are formed between the limits 0 and 55 per cent. of

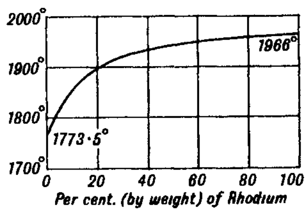


FIG. 64.—The Melting Points of the Rhodium-Platinum alloys.

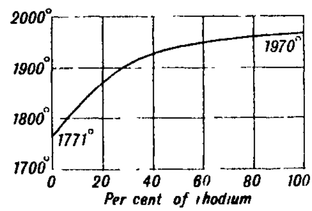


FIG. 65.—Freezing-point Curve of the Platinum-Rhodium Alloys.

rhodium. J. S. Acken's observations on the melting points are summarized in Fig. 64. W. Keitel and H. E. Zschiegner prepared platinum-rhodium electrolytically. L. Müller, and O. Feussner and L. Müller's results for the f.p. of mixtures of platinum and rhodium are summarized in Fig. 65. W. A. Nemiloff and N. M. Voronoff found that solid soln. are formed at all concentrations. J. Weerts represented the dimensions of the lattice parameter a of the face-centred cube by Fig. 66. K. Iokibe and S. Sakai found the viscosity of a platinum-rhodium alloy at 17° to be $4{\cdot}19\times10^8$;

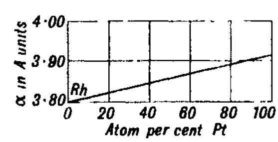


FIG. 66.—Lattice Parameters of the Rh-Pt Alloys.

and the rigidity, and logarithmic decrement, with a period of about 10 seconds :

	21°	174°	333°	497°	534°	610°
Rigidity $\times 10^{-11}$.	6·48	6·33	6·15	5·83	5·70	5·43
Log. decr. . .	$0{\cdot}0_320$	$0{\cdot}0_321$	$0{\cdot}0_237$	$0{\cdot}0_272$	0·0136	—

G. K. Burgess and co-workers observed that the presence of rhodium reduces the loss in weight of platinum by volatilization at temp. exceeding 900°, so that best quality platinum crucibles might have 3 to 5 per cent. of rhodium and be free from iron, iridium, and other impurities. The sp. gr. of the alloys by J. S. Acken are

summarized in Fig. 67, and their hardness, in the same diagram. W. A. Nemiloff and N. M. Voronoff found the Brinell's hardness of the alloy to be :

Rhodium . .	0	70	20	40	60	80	90	100 at. per cent.
Hardness . .	28·00	56·87	67·73	71·41	75·83	47·60	73·47	54·91

Rhodium is sometimes added to platinum for hardening platinum, and such alloys retain their hardness even after long exposure at a high temp.—*vide* Table IV. An alloy with 20 per cent. of rhodium has been recommended as wire for high temp. resistance furnaces. The alloys have a lower rate of volatilization than platinum, and they do not crystallize so readily. They are therefore preferred to platinum alone for crucible and some thermoelectric work. An alloy with 3½ per

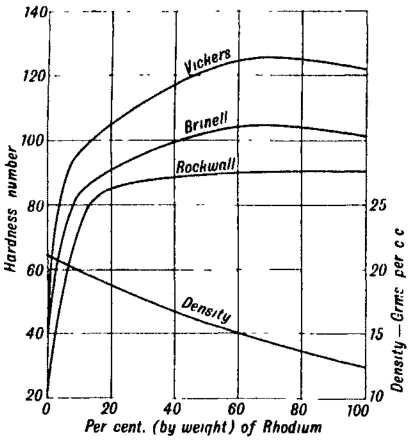


FIG. 67.—The Density and Hardness of the Rhodium-Platinum Alloys.

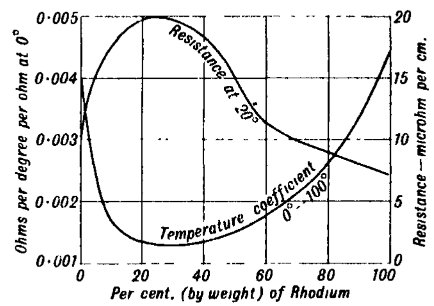


FIG. 68.—The Electrical Resistance and its Temperature Coefficient of the Rhodium-Platinum Alloys.

cent. of rhodium is in use. E. R. Thews, and I. E. Adaduroff discussed some uses of the alloys. F. E. Carter observed that alloys with up to 50 per cent. of rhodium can be worked, but those with higher percentages work with difficulty. Rhodium does not harden platinum so much as ruthenium, or iridium, but it hardens the metal more than palladium. The Brinell's hardness, H, the tensile strength in kgrms. per sq. mm., the resistance R ohms per million ft., and the temp. coeff. a per degree between 0° and 1200°, are :

Rhodium . . .	3·5	10	20	50 per cent.
Hardness . . .	107	165	211	323
Annealed 1000° . .	—	—	169	254
Annealed 1200° . .	65	90	107	138
R	103	110	125	134
a	0·00195	0·00135	0·00120	

T. Barratt and R. M. Winter found the thermal conductivity of an alloy with 10 per cent. rhodium to be 0·072 Cal. per cm. per sec. per degree at 17°, and 0·073 at 100°. The electrical resistance, and the temp. coeff. of the resistance of the alloys observed by J. S. Acken, are indicated in Fig. 69. W. A. Nemiloff and N. M. Voronoff found the sp. resistance, $R \times 10^6$, to be, at 25° and 100° :

Rhodium	0	10	20	30	40	50	60	100 at. %
$R \times 10^6$ 25°	10·88	16·97	19·69	20·40	19·83	17·95	16·35	6·02
$R \times 10^6$ 100	13·79	19·64	22·03	22·42	22·07	19·70	18·09	—
Temp. coeff.	0·00392	0·00221	0·00165	0·00136	0·00156	0·00134	0·00147	—

J. L. R. Morgan and O. M. Lammert studied electrodes made of this alloy in electrometric titrations. J. L. R. Morgan and co-workers studied the reproducibility of the quinhydrone electrode with platinum-rhodium. R. B. Sosman,

A. L. Day and R. B. Sosman found the thermoelectric force, *E* millivolts, of the alloys against platinum to be :

Pt : Rh	0°	200°	400°	600°	800°	1000°	1200°	1400°	1600°
95 : 5	0	0·55	2·53	3·92	5·33	6·79	8·20	9·82	11·31
90 : 10	0	0·64	3·25	5·23	7·33	9·57	11·93	14·34	16·75
85 : 15	0	0·65	3·45	5·71	8·23	10·96	13·87	16·89	19·94

Observations were also made by L. H. Adams, C. Barus, K. Bito and M. Matsui, V. N. Bozhovsky and B. V. Drozdoff, H. le Chatelier, A. L. Day and L. Holborn, J. Dewar and J. A. Fleming, J. Galibourg, W. Goedecke, L. Holborn and S. Valentiner, L. Holborn and W. Wein, T. Nakada, W. A. Nemiloff and N. M. Voronoff, A. L. Norbury, W. F. Roeser and H. T. Wensel, S. Schulze, A. W. Smith, J. C. Southard and R. T. Milner, F. Stäblein and J. Hinnüber, and C. W. Waidner and G. K. Burgess. F. R. Caldwell found the thermal e.m.f. of purified platinum against platinum-rhodium alloys, in millivolts, to be as indicated in Table V.

TABLE V.—THERMOELECTRIC FORCE IN MILLIVOLTS OF PLATINUM AGAINST PLATINUM-RHODIUM ALLOYS.

Temperature	Per cent. rhodium								
	0·1	1·0	10·0	21·6	39·0	56·6	61·2	80·7	100
50°	0·009	0·088	0·298	0·280	0·295	0·304	0·298	0·296	0·314
100°	0·020	0·180	0·643	0·621	0·651	0·676	0·672	0·623	0·696
200°	0·042	0·372	1·436	1·443	1·515	1·592	1·590	1·492	1·606
400°	0·087	0·758	3·249	3·500	3·700	3·914	3·920	3·770	3·915
600°	0·130	1·128	5·221	5·936	6·356	6·732	6·747	6·602	6·772
800°	0·171	1·489	7·331	8·702	9·446	9·996	10·028	9·931	10·158
1000°	0·213	1·852	9·570	11·771	12·960	13·714	13·776	13·745	14·050
1200°	0·254	2·218	11·922	15·121	16·876	17·863	17·986	18·024	18·432

L. Holborn and F. Henning found that the loss in weight of the thermocouple near the m.p. is less with platinum-rhodium alloys than it is with platinum-iridium alloys. W. Broniewsky discussed the thermoelectric properties of the alloys.

According to E. Matthey, C. Barus, and J. Dewar and J. A. Fleming, alloys containing less than 5 per cent. of rhodium are soluble in aqua regia ; but alloys with over 30 per cent. of rhodium are insoluble in aqua regia, and fuse more readily than rhodium itself. V. A. Nemiloff and N. M. Voronoff found the alloys are not corroded by acids, but at 750° alloys with over 10 per cent. of rhodium are oxidized by air. At higher temp. the oxide is decomposed, and no oxidation occurs above 1150°. For example :

Rhodium		10	20	30	40	50	60 at. per cent.
Surface area		8·5	9·6	11·0	7·7	4·8	5·9 sq. cm.
Weight	Before calcination	1·3906	1·4830	2·0192	1·2312	0·8160	0·9600 grm.
	Calcined at 750°	1·3906	1·4831	2·0193	1·2318	0·8164	0·9606 ,,
	Calcined at 1150°	1·3905	1·4829	2·0192	1·2312	0·8162	0·9603 ,,

G. R. Levi found that the presence of 10 per cent. of rhodium diminished the catalytic activity of platinum in hydrogen dioxide. A rhodium-platinum gauze has been recommended as a catalyst in the oxidation of ammonia.

R. Chenevix [23] prepared a **platinum-palladium alloy** from equal weights of the two metals at a temp. a little below the m.p. of palladium. The grey alloy had the hardness of bar iron ; a ductility less than that of a gold-palladium alloy ; and a sp. gr. of 51·141. J. A. M. van Liempt studied the alloys. C. L. Utterback studied the contamination of palladium when it is heated in contact with

platinum. G. Tammann and H. J. Rocha observed that alloys with less than 30 per cent. of palladium have a granular structure and those with more than 40 per cent. of palladium have a dendritic structure. E. R. Thews discussed some uses of the alloys. There appears to be a continuous series of solid soln. T. Barth and G. Lunde studied the lattice constant of the alloys. G. Tammann and H. J. Rocha observed that the maximum hardness of the alloys occurs at 10 to 20 per cent. of palladium when the alloys are quenched from 1400°, at 30 per cent. when they are quenched from 1200°, and at 40 per cent., when they are annealed at 600° for 12 hrs.—*vide* Table IV. Quenched alloys, except that containing 38 per cent. of palladium, are all harder than annealed alloys. F. Goldberger and O. Kienberger, and N. S. Kurnakoff studied the streak as an indication of the composition of the alloy. W. Geibel obtained the results indicated in Fig. 69 for the tensile strength in kilograms for a wire of diameter 1 mm. The

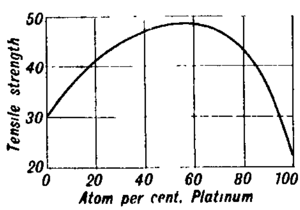


FIG. 69.—The Tensile Strength of the Palladium-Platinum Alloys.

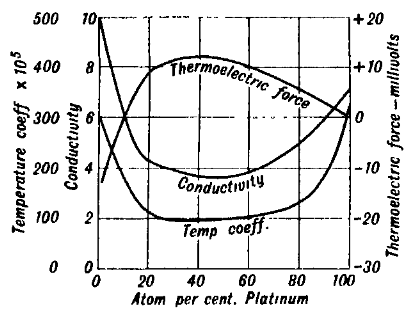


FIG. 70.—The Electrical Properties of the Platinum-Palladium Alloys.

subject was studied by E. M. Wise and J. T. Eash. According to F. E. Carter, palladium does not harden platinum in the same way as do the other metals of the group, and a whole series of homogeneous alloys can be formed which are easily workable. The alloy of maximum hardness has about 25 per cent. of palladium. The Brinell hardness, *H*, Ericson's ductility test, and the electrical resistance, *R* ohms per million ft., are as follows:

Palladium	10	20	25	50	75 per cent.
H Hard	160	170	175	165	155
H Annealed	85	95	100	90	80
Ductility	11·1	11·5	8·1	7·9	9·5
R	130	160	170	180	145

The values for the electrical conductivity $\times 10^{-4}$ at 0° and its temp. coeff. between 0° and 160° are indicated in Fig. 70; and the thermoelectric force of the alloys against platinum, expressed in millivolts, are summarized in Fig. 71. C. Barus made observations on the electrical resistance of the alloys. L. Holborn and A. L. Day found the thermoelectric force, *E* millivolts, of the couples:

Pt : Pd	−185°	0°	200°	400°	600°	800°	1000°	1200°
90 : 10	−0·11	0	0·62	1·48	2·42	3·35	4·78	5·25
10 : 90	—	0	−0·31	−0·35	0·12	1·2	4·2	—

Observations were made by A. W. Smith, R. von D. Wegner, and J. Monheim. E. Vogt studied the magnetic properties of the platinum-palladium alloys; and Y. Shimizu gave for the magnetic susceptibilities, χ, in mass units:

Platinum	100·00	95·96	82·24	75·24	67·38	50·09	41·39	11·90	0 per cent.
$\chi \times 10^6$	1·08	1·12	1·32	1·41	1·60	2·19	2·55	4·25	5·20

G. Borelius studied the diffusion of hydrogen in the alloy.

A. Sieverts and co-workers, and G. Borelius studied the absorption of hydrogen by the platinum-palladium alloys, and found that the solubility, S, is proportional

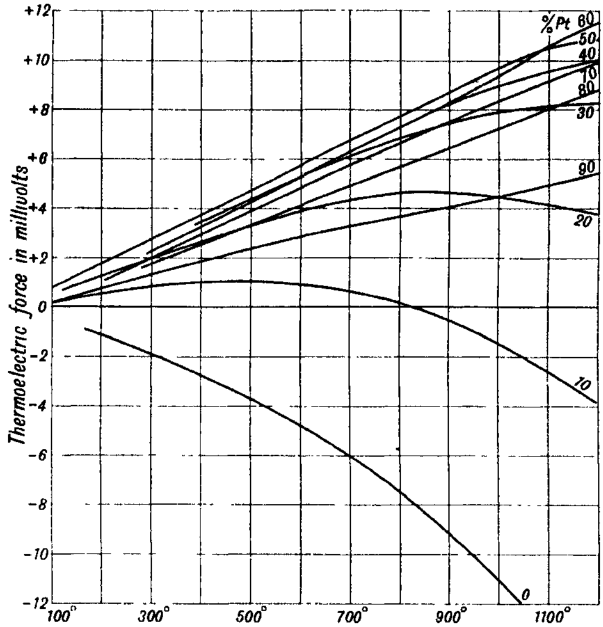


FIG. 71.—The Thermoelectric Force of the Platinum-Palladium Alloys against Platinum.

to the square root of the press., and it increases with rise of temp. The results are summarized in Fig. 72. G. Borelius and S. Lindblom studied the passage of hydrogen through the alloy. G. Tammann and H. J. Rocha observed that the solubility of hydrogen in the alloys is very small when less than 40 per cent. of palladium is present, and then increases rapidly with the palladium content. The solubility is slightly greater in alloys quenched from 1300° than it is in alloys annealed at 700°. Alloys with over 74 at. per cent. of palladium become coated with gold when immersed in a soln. of chloroauric acid, and those with over 50 per cent. of palladium are blackened by an alcoholic soln. of iodine. F. E. Carter said that the alloys have rather the character of platinum. Boiling nitric acid has no solvent action on alloys with up to 25 per cent. of palladium; nor do these alloys show the colour effect of palladium when heated. They are used to some extent in jewellery. G. R. Levi found that the presence of 10 per cent. of palladium diminished the catalytic activity of platinum on hydrogen dioxide; H. Remy and H. Gonnington, the hydrogen-oxygen reaction; and E. Decarrière, the catalytic activity of the alloys on the oxidation of ammonia.

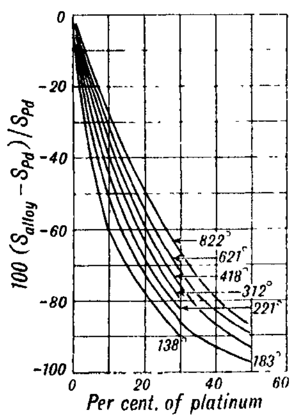


FIG. 72.—The Solubility of Hydrogen in Platinum-Palladium Alloys.

F. Korn [24] said that the **platinum-palladium-gold alloys** are used as a substitute for platinum, with the trade-name *pallas*; and F. E. Carter said that the **platinum-palladium-rhodium alloys** are useful for jewellery. W. C. Heraeus, and F. E. Carter found that with **platinum-osmium alloys** osmium has about

$2\frac{1}{2}$ times the hardening effect of iridium on platinum, and it also increases the electrical resistance $2\frac{1}{2}$ times as quickly. An alloy with over 10 per cent. of osmium is difficult to work owing to its hardness and lack of ductility—*vide* Table IV. The annealing must be done under reducing conditions or the osmium burns off. F. Zimmermann discussed the hardness of the alloys. H. Remy and B. Schäffer observed that osmium-platinum alloys are not very active catalysts in the reaction between hydrogen and oxygen, although separately the metals are active. H. Remy and H. Gonnington studied the subject. G. R. Levi observed that the presence of 10 per cent. of osmium almost doubled the catalytic activity of platinum on hydrogen dioxide. E. Haagn used an alloy with 40 to 60 per cent. of ruthenium, 35 to 50 per cent. of osmium, and 5 to 15 per cent. of platinum for tipping the nibs of fountain pens. F. E. Carter said that the **platinum-palladium-osmium alloys,** formerly used for jewellery, were abandoned in favour of the platinum-palladium-rhodium alloys because of the volatilization of osmium when heated—a subject discussed by C. M. Hoke.

G. Rose,[25] and A. Breithaupt described a native **platinum-iridium alloy** from the Urals. V. Rekschinsky discussed the separation of osmiridium (*q.v.*) from metals of the platinum group. J. J. Berzelius observed that equal weights of platinum and iridium form a brittle alloy which can be welded, and that the alloy with a small proportion of iridium is ductile and harder than iridium, and more resistant to high temperatures, and to chemical reagents. H. Morin, and A. Gaudin prepared alloys with 10 per cent. of iridium and found them to be malleable, and not to tarnish when employed as metallic mirrors on copper. B. S. Jacobi discussed the use of an alloy with 20 per cent. of iridium for medals. He said that the alloy can be cold-worked, and that it is hard, and is only slightly affected by aqua regia. O. J. Broch and co-workers, and H. St. C. Deville and H. Debray described the preparation of the platinum-iridium standard measure for the Comité International des Poids et Mesures. F. E. Carter noted iridium can be worked at high temp., but a little platinum induces brittleness. Iridium is employed to harden platinum to enable it to be used in chemical ware, electric work, and jewellery. In *medium hard* jewellery, the platinum contains 5 per cent. of iridium, and in hard jewellery, 10 per cent. The limit of workability is 30 to 35 per cent. of iridium. The alloys are solid soln., and any coring in the crystal grains can be rectified by annealing. Segregation does not usually occur. F. Korn, and E. A. Smith discussed the application of the alloys in the jewellery trade, etc. H. St. C. Deville and H. Debray found the sp. gr. of alloys with 10, 15, 33·3, and 95 per cent. of iridium to be respectively 21·615, 21·618, 21·874, and 22·384. T. Barratt and R. M. Winter gave for the thermal conductivity of alloys :

	17°			100°		
Per cent. iridium . . .	10	15	20	10	15	20
Cals. per cm. per sec. per degree .	0·074	0·056	0·042	0·075	0·059	0·042

O. Feussner and L. Müller, and L. Müller measured the f.p. of alloys of the two metals, and the results are summarized in Fig. 73. F. E. Carter said that the alloys do not oxidize above 1150°, but iridium slowly volatilizes from them ; a film of oxide forms when the alloy is cooled in the range 1150° to 900°. K. Friederich studied the magnetic properties of the alloys. They darken superficially when heated within the range 900° to 1100°, presumably owing to the formation of an oxide ; at a higher temp., the oxide is decomposed and the surface regains its colour. Iridium itself acquires a bluish film under similar conditions. The alloys begin to lose weight above 900° owing to the volatilization of the iridium oxide. Hence for high temp. gravimetric work iridium is objectionable in platinum crucibles, and in thermocouple work. F. Haber studied the resistance of platinum-iridium electrodes in the electrolysis of hydrochloric acid; and J. Lüke and R. Fricke, the decomposition of nitrous oxide by glowing wires of the alloy. B. S. Srikantan studied the reaction $H_2+CO_2 \rightleftharpoons CO+H_2O$ on platinum-iridium alloys ; H. Remy

and H. Gonnington, the hydrogen-oxygen reaction. W. A. Nemiloff discussed the microstructure of the alloys. W. A. Nemiloff's observations on the Brinell's

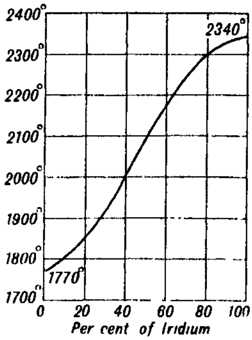


FIG. 73.—The Liquidus Curve of Platinum-Iridium Alloys.

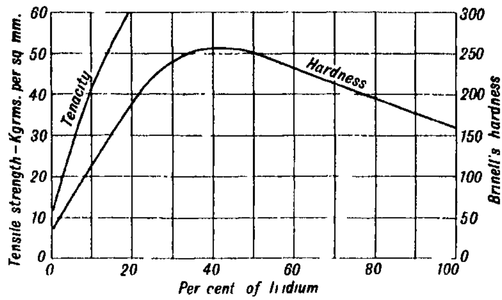


FIG. 74.—The Tensile Strength and Hardness of Platinum-Iridium Alloys.

hardness are summarized in Fig. 74, and the same diagram gives the tensile strength of the alloys in kgrms. per sq. mm.—*vide* Table IV. J. Weerts obtained the dimensions a of the parameters of the face-centred cubic lattice of the alloys shown in Fig. 75. F. Goldberger and O. Kienberger studied the streak as an indication of the composition of the alloy. W. Geibel observed that alloys made into wires 1 mm. diameter, had a breaking load, in kilograms, of

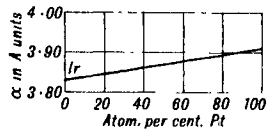


FIG. 75.—The Lattice Parameter of the Ir-Pt Alloys.

Iridium . .	0	5	10	15	20	25	30	35 per cent.
Load . .	24	40	48	66	81	98	114	126 kgrms.

E. Steinmann's results for the effect of annealing on the tensile strength are summarized in Fig. 76. K. B. Thews gave 40 kgrms. per sq. mm. for a 5 per cent. iridium alloy, and 100 kgrms. per sq. mm. for a 25 per cent. iridium alloy. E. M. Wise and J. T. Eash gave for the alloy with 20 per cent. iridium, reduced 50 per cent. by cold drawing, the ultimate strength 140,500 lbs. per sq. in., proportional limit 101,000 lbs. per sq. in., elongation 2·5 per cent. in 2 in., a reduction in area of 85 per cent.; after a softening anneal at 1400°, the ultimate strength was 93,500 lbs. per sq. in.; proportional limit, 59,500 lbs. per sq. in.; elongation, 20 per cent. in 2 ins., and reduction of area, 88 per cent. F. E. Carter gave for Brinell's hardness, H, Ericson's ductility test in mm.; and the resistance, R ohms per million feet:

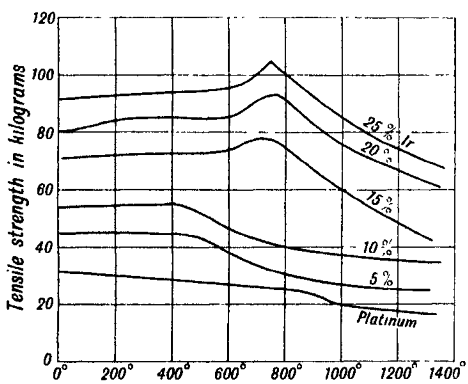


FIG. 76.—The Effect of the Annealing Temperature on the Tensile Strength.

Iridium	0	5	10	15	20	25	30 per cent.
H Hard . . .	97	170	220	280	330	370	400
H Annealed . . .	47	110	150	190	230	270	310
Ductility Hard . .	7·8	7·1	7·1	7·0	7·0	4·1	—
Ductility Annealed 1100°	12·2	10·7	10·0	9·7	9·0	8·0	—
Ductility Annealed 1200°	12·2	10·7	10·4	10·2	9·7	7·8	2·0
R	60	120	160	185	200	210	210

The ductility data show that with increasing iridium content, higher annealing temp. are required. The hard-worked alloys do not show a very marked difference in ductility until over 20 per cent. is attained, when there is a decrease. F. Korn, and N. S. Kurnakoff studied the subject.

A. E. Tutton measured the coeff. of thermal expansion of a platinum-iridium alloy. W. A. Nemiloff measured the sp. electrical resistance, R, of some alloys at 25°, and 100°, and obtained :

Iridium		0·25	1	2	5	10	20 per cent.
$R\times10^6$	25°	11·948	14·894	14·792	22·773	24·349	30·685
	100°	14·838	17·590	17·605	25·376	26·705	32·710

The results at 25°, and the temp. coeff. of the binary alloys between 25° and 100° are indicated in Fig. 77. L. Guillet and M. Ballay observed a slight increase in the resistance when the alloy is cold-worked and annealed at 950°. J. Obata studied the effect of a magnetic field, and J. L. R. Morgan and co-workers, the

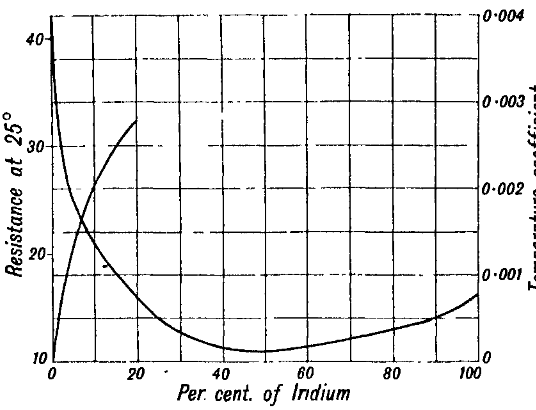


FIG. 77.—The Electrical Resistance of the Platinum-Iridium Alloys.

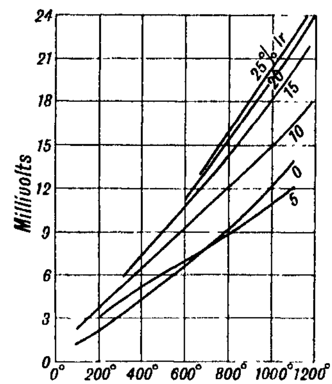


FIG. 78.—The Thermoelectric Force of the Platinum-Iridium Alloys.

reproducibility of quinhydrone electrodes with platinum-iridium electrodes. W. Geibel, R. von D. Wegner, W. Broniewsky, W. H. Keesom and J. N. van Ende, and J. W. Schmidt measured the thermoelectric force of the alloys. The results are summarized in Fig. 78. B. Brenner, C. W. Waidner and G. K. Burgess, H. le Chatelier, and C. Barus made some observations on the subject. J. Lüke and R. Fricke studied the action of the alloy on nitrous oxide. P. G. Tait gave $dE/d\theta=7{\cdot}90+0{\cdot}0062\theta$ microvolts per degree for lead against alloys with 15 per cent. of iridium, $5{\cdot}90-0{\cdot}0133\theta$ for alloys with 10 per cent. iridium, and $6{\cdot}15+0{\cdot}0055\theta$ for alloys with 5 per cent. iridium; and the corresponding neutral points are respectively −1274°, 444°, and −1118°. F. Haber found that the alloy with 10 per cent. iridium is scarcely attacked when used as anode in the electrolysis of hydrochloric acid, and the alloy with 20 per cent. is not attacked at all. G. R. Levi observed that the presence of 10 per cent. of iridium decreased the catalytic activity of platinum on hydrogen dioxide. M. Delépine noted the dissolution of the platinum-iridium alloy in sulphuric acid at the rate of 0·10 grm. per hour per sq. dm. at 265°.

H. St. C. Deville and H. Debray discussed the **platinum-iridium-rhodium alloy** which occurs as " a triple alloy of an invariable composition " ; and they prepared the quaternary **platinum-iridium-rhodium-tin alloy.** F. E. Carter said that the platinum-iridium-rhodium alloys are used for radio tubes. The **platinum-iridium-osmium alloys** are used for sparking plugs. C. O. Bannister and E. A. du Vergier discussed the analyses of the platinum-iridium alloys.

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§ 17. The Lower Oxides of Platinum and their Hydrates

P. Klason [1] observed that when a hot soln. of potassium chloroplatinite is evaporated, platinic chloride, and a derivative of a lower oxide, probably **platinum suboxide,** or **platinum hemioxide,** Pt_2O, are formed. G. Neumann said that J. W. Döbereiner's datum on the amount of oxygen occluded by platinum corresponds with 3·05 per cent., and that the value calculated for Pt_2O is 3·85 per cent. This is probably a coincidence, although it has been taken to be an indication that a hemioxide is formed. P. T. Cleve prepared **platinous dihydroxytetrammine,** $Pt_2(NH_3)_4(OH)_2$, by boiling platinous *cis*-dichlorotetrammine with soda-lye, and drying the product at 100°. The dirty white powder is insoluble in water; hydrochloric acid forms a mixture of *cis*-dichlorodiammine and dichlorotetrammine; whilst nitric and sulphuric acids form the corresponding nitrate and sulphate; and aqua regia forms platinic tetrachlorotetrammine. C. W. Blomstrand discussed the nature of the compound.

W. Manchot and G. Lehmann treated a 1 per cent. aq. soln. of potassium platinocyanide with 3 per cent. sodium amalgam, and obtained a colourless solution which reduced an ammoniacal soln. of silver, cadmium salt soln., mercuric chloride, bismuth salt, litmus, anthraquinonesulphonate, and acidic indigotin. If exposed to air, the reducing power of the soln. slowly disappears. Reduction can also be effected by potassium amalgam, calcium filings, electrolytically, or by aluminium and potassium hydroxide. Barium platinocyanide may be used or potassium chloroplatinite or chloroplatinate in presence of the equivalent amount of potassium cyanide. Attempts to concentrate the reduced soln. on a water-bath or in vacuo are accompanied by an evolution of gas, and potassium platinocyanide separates. The soln. is supposed to contain univalent platinum.

According to L. Gmelin, **platinum monoxide** or **platinous oxide,** PtO, is probably formed during the "combustion" of platinum which occurs at the m.p. and which is attended with sparking, the emission of fumes, and the formation of a dirty green dust. The "combustion" does not occur at an ordinary white heat, but only in the oxyhydrogen flame, the oxy-alcohol flame, or when a thin platinum wire is explosively spluttered by an electric current. The alleged nature of the product is very doubtful. According to L. Wöhler,[2] the oxygen associated with platinum black is probably present in great part as platinous oxide or its hydrate. The preparation of oxygenated spongy platinum is best conducted at 510°, and not above 560°. P. Laffitte and P. Grandadam obtained the oxides PtO and PtO_2 by heating the metal in oxygen to 100° to 560° at a press. of 8 to 200 atm. W. F. Bruce discussed the subject. J. J. Berzelius said that the hydrate can be deprived of its water by a gentle heat; and C. Engler and L. Wöhler added that the water is difficult to drive off, and requires a temp. of at least 300°. L. Wöhler found that the expulsion of the water is attended by some decomposition of the oxide so that the pure oxide free from hydrate cannot be so prepared. J. W. Döbereiner heated calcium chloroplatinate, $Ca_2Pt_2O_5Cl_2.7H_2O$, in a covered crucible, and obtained a violet powder which becomes very hot when treated with water; the lime and calcium chloride can be removed by water and dil. nitric acid, and there remains platinous oxide.

J. W. Döbereiner's product is a violet powder; J. J. Berzelius' product is a grey powder; and L. Wöhler's, velvety black. P. Laffitte and P. Grandadam gave 14·9 for the sp. gr. at 15°. H. G. Howell and G. D. Rochester studied the band spectrum. L. Wöhler said that platinous oxide is perceptibly decomposed at 430°; P. Laffitte and P. Grandadam said that it decomposes at 560°; and, according to J. J. Berzelius, the oxide is completely decomposed at a red-heat so that the product of the operation above cited by L. Gmelin is not likely to have been the monoxide. J. J. Berzelius also observed that when the monoxide is mixed with powdered charcoal, and heated to redness, there is a strong detonation. L. Wöhler observed that the oxide very slowly dissolves in boiling hydrochloric

acid, and that the rate of dissolution is catalytically increased in the presence of a trace of platinous chloride, or of a soln. of platinous hydroxide in hydrochloric acid. J. W. Döbereiner found that the monoxide dissolves in sulphurous acid, but not in the other oxyacids; and L. Wohler, that it is a little soluble in aqua regia. L. F. Nilson obtained **platinous nitrosyl oxides,** $(Pt.O.ON : ON.OH)_2O$; and also $Pt_3H_4(NO_2)_8O.2H_2O$; and J. Lang, $H_2Pt(NO_2)_4$. F. Mylius and F. Förster obtained evidence indicating the formation of **platinous carbonyl oxide,** or **platinous oxycarbonyl,** [Pt(CO)O], or CO.PtO. J. W. Döbereiner observed that formic acid reduces the oxide to platinum black with a violent evolution of carbon dioxide; and that it takes up some oxalic acid from a boiling aq. soln. F. D. Aguirreche hydrogenized salicylic acid using platinum oxide as catalyst.

As indicated above, L. Wöhler showed that the oxygen associated with ordinary platinum black is in part present as **hydrated platinous oxide,** $PtO.nH_2O$. J. J. Berzelius prepared it by gently warming platinous chloride with a soln. of potassium hydroxide, and washing the precipitate. Part of the platinum monoxide is dissolved by the alkali-lye which is in consequence coloured green, and it can be recovered from the soln. by the addition of sulphuric acid. J. von Liebig added that the hydrated oxide so obtained is contaminated with chloride, and if too much potash-lye be present, the precipitate redissolves. E. von Meyer recommended using a small excess of potash-lye, and drying the carefully-washed product at 105° to 110°. L. N. Vauquelin observed that if soda-lye be employed for the precipitation, the precipitated hydrate is contaminated with soda which cannot be removed by washing. J. Thomsen boiled a soln. of a mol of potassium chloroplatinate in 300 mols of water with 2 mols of a dil. soln. of sodium hydroxide, and washed the black precipitate first by decantation, and afterwards on a filter— L. Mond and co-workers observed that the product is always contaminated with chlorides, and L. Wöhler, that it has a tendency to oxidize unless it is washed in an atm. of an inert gas—say carbon dioxide—and dried in a desiccator first filled with carbon dioxide, and afterwards evacuated. F. Martin, and L. Wöhler and F. Martin prepared the hydrated oxide by dropping a soln. of sodium carbonate into one of potassium chloroplatinite—or of a soln. of hydrochloroplatinic acid which has been treated with sulphur dioxide—and boiling the liquid in an atm. of carbon dioxide until the black, hydrated oxide is precipitated; the product is again boiled with a soln. of sodium carbonate to remove the chlorides from the precipitate which is then washed and dried as before.

The hydrated monoxide is a black powder which, according to L. Wöhler, has the composition of a *monohydrate*, or **platinous hydroxide,** $Pt(OH)_2$, if it has been dried for a sufficient length of time at 100°. L. Wöhler and F. Martin considered this hydrate to be **platinous acid,** H_2PtO_2, which forms salts, **platinites.** J. Thomsen obtained the hydroxide by boiling a dil. aq. soln. of potassium chloroplatinite with the proper proportion of soda-lye; and L. Wöhler and W. Frey, by boiling in an atm. of carbon dioxide a soln. of potassium chloroplatinite mixed with the calculated quantity of sodium hydroxide, boiling the precipitate several days in water, and drying in an atm. of carbon dioxide for 48 hrs. at 120° to 150°. The precipitate obtained at ordinary temp. approximates to the *dihydrate*, $PtO.2H_2O$. J. J. Berzelius stated that when potassium hydroxide is fused in a platinum vessel, out of contact with air, **potassium platinite** is formed, and it yields a dark soln. in water. Likewise when platinous chloride is decomposed by potash-lye, a dark green soln. of potassium platinite is formed. L. N. Vauquelin obtained what was regarded as **sodium platinite** by decomposing a soln. of platinous chloride with an excess of soda-lye.

Kalle and Co. prepared **colloidal platinous hydroxide** by mixing a dil. soln. of sodium protalbinate and sodium carbonate with a dil. soln. of platinous chloride and sodium acetate, and warming the mixture on a water-bath at 70° to 80°. The dialyzed soln. on evaporation furnishes dark green plates which form a colloidal soln. with water. A. Skita and W. A. Meyer used gum arabic as protective colloid.

L. Mond and co-workers observed that hydrated platinous oxide loses the greater proportion of its water at 200° to 250°; and C. Engler and L. Wöhler added that the last traces of water are driven off with difficulty, and a temp. over 300° is required. L. Wöhler observed that after heating 2 days on a water-bath, the hydrate contained 13·4 per cent. of water, and 8·5 per cent. of oxygen; after heating 14 days at

	250°	300°	400°	
Water, H_2O	13·4	8·4	—	per cent.
Oxide oxygen	8·5	8·5	7·4	,,

The calculated oxygen for PtO is 7·6, and the calculated H_2O for $Pt(OH)_2$ is 6·3 per cent. L. Mond and co-workers found that oxygen is lost between 237° and 360°, and that after removing water, the platinous oxide gives off water very slowly at 380°; and at 440° the greater part of the oxygen can be gradually pumped off, but a red-heat is necessary to remove all the oxygen. The subject was studied by J. Thomsen. L. Wöhler found that in vacuo, or in an atm. of carbon dioxide, decomposition begins at 400°, but no decomposition is perceptible at 365°. The velocity of decomposition decreases with decreasing proportions of water. Platinum monoxide decomposes when heated into platinum and platinum dioxide, which dissolves in the monoxide lowering its dissociation press. Thus, a sample of monoxide at 510° gave a dissociation press. of 752 mm., which in 40 hrs. decreased to 203 mm. J. Thomsen gave for the heat of formation: $2Pt+O_2+2H_2O = 2Pt(OH)_2+38{\cdot}44$ Cals. M. le Blanc and H. Sachse said that the conductivity of the oxide is small.

Chemical properties of platinous oxide.—E. von Meyer observed that **hydrogen** reduces the oxide with great energy; and L. Wöhler, that the oxide, dried at ordinary temp. or at 100°, reacts vigorously with hydrogen. E. von Meyer observed that the monoxide oxidizes hydrogen rather more vigorously than does platinum dioxide. The reaction was studied by A. R. Ubbelohde. L. Wöhler showed that the oxide explodes in an electrolytic mixture of hydrogen and oxygen. L. Mond and co-workers found that the oxide adsorbs oxygen; and L. Wöhler and co-workers, that the freshly-precipitated and moist oxide may adsorb 2 per cent. of **oxygen**; but the dried oxide, even if exposed to oxygen under 100 atm. press. for some hours, adsorbs no perceptible quantity of oxygen, but it is oxidized in a short time at 100°. A suspension of the monoxide in boiling water does not form the hemitrioxide when oxygen is passed through the liquid for 2 days; the monoxide, however, is oxidized by **ozone.** C. Engler and L. Wöhler observed that **hydrogen dioxide** is reduced completely when boiled with platinum monoxide, but not perceptibly in the cold. The hydrated oxide is easily soluble in cold **hydrochloric acid,** and, according to J. J. Berzelius, hydrochloroplatinic acid and metal are formed. L. Wöhler found that the air-dried oxide is not easily soluble in $2N$-HCl. If heated on the water-bath the oxide becomes still less soluble in hydrochloric acid, and after the monoxide has been heated to 300° or 400°, platinous oxide can be boiled for an hour with conc. hydrochloric acid, or aqua regia, without perceptible change, dissolution occurs slowly with a more protracted boiling. L. Wöhler said that when hydrochloric acid acts on the hydrated oxide, there are two concurrent reactions: (i) $Pt(OH)_2+4HCl=H_2PtCl_4+2H_2O$, and (ii) $2Pt(OH)_2 = Pt(OH)_4+Pt$, followed by $Pt(OH)_4+6HCl=H_2PtCl_6+4H_2O$. The first of the concurrent reactions progresses more rapidly than the second. J. Thomsen noted that the hydrated oxide is freely soluble in **hydrobromic acid**; and L. Wöhler, and J. Thomsen found that platinum monoxide oxidizes **hydriodic acid.** W. Plüddemann, and L. Wöhler and co-workers observed that the reduction of platinum monoxide by **sulphur dioxide** begins at 130°, proceeds vigorously at 200°, and is very rapid at 400°. L. Wöhler also showed that the hydrated oxide is readily soluble in **sulphurous acid** to form, according to C. Engler and L. Wöhler, a reddish-brown liquid, and a little metallic platinum. L. Wöhler observed that the freshly-precipitated and moist hydrated oxide is very sparingly soluble in **sulphuric acid,** and similarly

with the hydrated oxide dried in a desiccator, but when dried at 110°, it is soluble in fuming sulphuric acid at 200°. The dry or moist hydrated oxide is virtually insoluble in **nitric acid.** It transforms **arsenic trioxide** into the pentoxide. C. Engler and L. Wöhler found that **carbon monoxide** reduces platinous oxide to platinum; and E. von Meyer observed that it oxidizes carbon monoxide at ordinary temp. more readily than does platinum dioxide. P. V. McKinney and co-workers studied the reaction. J. Thomsen observed that **formic acid** reduces the oxide to metal with the evolution of carbon dioxide. F. Bullnheimer observed that platinum oxide is reduced to the metal by **glycerol.** L. Wöhler observed that the freshly-precipitated and moist hydrated oxide is virtually insoluble in dil. or conc. **acetic acid.** Boiling soln. of acetic acid, **oxalic acid,** and other organic acids are oxidized by the hydrated monoxide with the evolution of carbon dioxide. A boiling soln. of **glucose** is similarly oxidized. The hydrated oxide is soluble in a soln. of **potassium cyanide.** C. Engler and L. Wöhler noted that **tincture of guaiacum,** and **diphenylamine** are oxidized. According to J. J. Berzelius, the hydrated monoxide is decomposed by a boiling soln. of **potasium hydroxide,** forming potassium platinate and metal. L. Wöhler observed that the moist oxide is scarcely soluble in a soln. of **sodium hydroxide,** although it is not precipitated from salt soln. by an excess of that alkali lye. A boiling sulphuric acid soln. of **potassium permanganate** is reduced to manganese dioxide, and platinum dioxide is formed.

Derivatives of the three types of ammines have been obtained, namely, the di-, tri-, and tetra-ammines. J. Reiset [3] prepared **platinous tetramminohydroxide,** $[Pt(NH_4)_4](OH)_2$, by adding the theoretical proportion of baryta water to a soln. of platinous tetramminosulphate, evaporating the filtrate out of contact with air, and finally in vacuo over sulphuric acid until it solidifies. The mass of white, acicular crystals is deliquescent in air. It melts at 110° and loses with intumescence 2 mols. of ammonia and 1 mol. of water so that $Pt(NH_3)_2O$ remains. J. Thomsen gave for the heats of neutralization of 2 eq. of an aq. soln. with sulphuric acid be 30·84 Cals., and with hydrochloric acid, 27·29 Cals. The mol. conductivities of a mol of the compound in 500, 1000, and 2000 litres were found by A. Werner and A. Miolati to be, respectively, 247·6, 260·8, and 267·2. G. Bredig gave 74·1 for the speed of migration of the $\frac{1}{2}[Pt(NH_3)_4]^{\cdot\cdot}$-ion. J. Reiset said that the aq. soln. has an alkaline, and caustic taste, and does not give off ammonia when boiled; the aq. soln. absorbs carbon dioxide from the atmosphere, and, like a soln. of potassium hydroxide, it decomposes starch-sugar; and like a soln. of potassium hydroxide, it precipitates silver oxide from a soln. of silver nitrate. M. Peyrone observed that the compound is slightly soluble in alcohol. It forms salts when treated with acids. It has been called *Reiset's first base,* when $[Pt(NH_3)_2](OH)_2$ represents Reiset's second base. The constitution was discussed by C. W. Blomstrand, H. and A. Euler, C. Gerhardt, W. Odling, C. Weltzein, and A. Werner.

W. Odling prepared **platinous dihydroxydiammine,** $[Pt(NH_3)_2(OH)_2]$, by the action of baryta water on the corresponding sulphate. The salt crystallizes easily, it is very soluble in water, forming a strongly alkaline soln., which attacks carbon dioxide from the atmosphere. The base is neutralized by acids, and the resulting salts readily form complexes with other metal salts. A. A. Grinberg, and A. A. Grinberg and D. I. Ryabchikoff studied the strength of these bases. P. Klason obtained acicular crystals of the dihydrate. The aq. soln. is feebly acidic. H. D. K. Drew and co-workers studied the α- and β-forms of this base. A. Werner obtained **platinous hydroxytriamminohydroxide,** $[Pt(NH_3)(OH)]OH$; and F. W. Pinkard and co-workers reported **platinous dihydroxylaminodiamminohydroxide,** $[Pt(NH_3)_2(NH_2OH)_2](OH)_2$; and F. Hoffmann, **platinous dihydroxylaminehydroxide,** $[Pt(NH_2OH)_2(OH)_2]$. J. Reiset obtained **platinous oxydiammine,** $[Pt(NH_3)_2O]$, by heating the tetramminehydroxide at 110°. The grey mass decomposes at 195° into platinum, nitrogen, ammonia, and steam. When heated in air to about 200°, it decomposes with a hissing noise. It is insoluble in water, and in aq. ammonia; with acids, it furnishes insoluble, explosive products.

H. Alexander prepared **platinous tetrahydroxylaminehydroxide,** $[Pt(NH_2OH)_4]$-$(OH)_2$, by treating the corresponding chloride with a strong base; R. Uhlenhut, by treating hydrochloroplatinic acid with a soln. of hydroxylamine; H. Wolfram, by the action of hydroxylamine on a soln. of hydrochloroplatinous acid; and N. Tarugi, by the action of an ammoniacal soln. of hydroxylamine hydrochloride on a conc. soln. of platinic chloride. The compound forms white, yellowish, or reddish-violet powder, or white acicular crystals. After drying at 80°, H. Wolfram found that the salt is brownish-yellow; H. Alexander said that the salt partially decomposes at 100°; and R. Uhlenhut, that it darkens at 169°, and explodes about 173°. H. Alexander, and R. Uhlenhut found that the salt is insoluble in hot or cold water; easily soluble in mineral acids, but it requires warm sulphuric acid for dissolution, and it is decomposed by the conc. acid. The base is insoluble in alcohol, and ether; it is soluble in formic and acetic acids; and the hydrochloric acid soln. reduces Fehling's soln. and also gold chloride soln. in the cold. The base forms salts with acids. The constitution was discussed by A. Werner. P. Klason, and W. Odling obtained the cis- and trans-forms of this base. P. T. Cleve prepared **platinous tetramminodihydroxide,** $Pt_2(NH_3)_4(OH)_2$, by the action of a boiling soln. of sodium hydroxide on platinous *cis*-dichlorodiammine, and drying the washed product at 100°; the dirty white powder explodes above 100°. It is insoluble in water and is converted by acids into salts. F. Hoffmann prepared **platinous dihydroxylaminediamminohydroxide,** $[Pt(NH_3)_2(NH_2OH)_2](OH)_2$, from the corresponding chloride; he also prepared **platinous dihydroxylamine-bispyridinehydroxide,** $[Pt(NH_2OH)_2(C_5H_5N)_2](OH)_2$, as a double salt with platinous chloride. A. Werner obtained **platinous bispropylenediaminehydroxide,** $[Pt\{C_3H_6(NH_2)_2\}_2](OH)_2$. H. Wolfram, H. Alexander, and F. Hoffmann prepared cis- and trans-forms of **platinous dihydroxydihydroxylamine,** $[Pt(NH_2OH)_2(OH)_2]$; H. Wolfram also prepared **platinous oxyhydroxylaminoethylamineoxide,** $2[Pt(NH_2OH)_2O][Pt(NH_2OH)(C_2H_5NH_2)O]$.

S. G. Hedin prepared **platinous quaterpyridinehydroxide,** $[Pt(C_6H_5N)_4](OH)_2$; he also prepared the cis- and trans-forms of **platinous dihydroxybispyridine,** $[Pt(C_5H_5N)_2(OH)_2]$, as well as the *dihydrate* and the *decahydrate*. This compound in its α- and β-forms was studied by H. D. K. Drew and co-workers. C. W. Blomstrand, and C. Enebuske described the trans-form of **platinous bismethylsulphinedihydroxide,** $[Pt\{(CH_3)_2S\}_2(OH)_2]$; C. W. Blomstrand, the trans-form of **platinous bisethylsulphinedihydroxide,** $[Pt\{(C_2H_5)_2S\}_2$-$(OH)_2]$; C. Rudelius, the trans-form of **platinous bispropylsulphine dihydroxide,** $[Pt\{(C_3H_7)_2S\}_2(OH)_2]$; C. W. Blomstrand, and H. Löndahl., **platinous bis *iso* butylsulphine-dihydroxide,** $[Pt\{(C_4H_9)_2S\}_2(OH)_2]$; F. G. Angell and co-workers, and H. Löndahl, **platinous bisethylenesulphinedihydroxide,** $[Pt\{S(C_2H_4)_2S\}(OH)_2]$; N. S. Kurnakoff, **platinous bisthiocarbamidebispyridinehydroxide,** $[Pt(C_5H_5N)_2\{CS(NH_2)_2\}_2](OH)_2$; G. Quesneville, M. G. Saillard, P. Schützenberger, and P. Schützenberger and M. G. Saillard, **platinous dihydroxytoluidinethylphosphitehydroxide,** $[Pt(C_7H_7NH_2)\{P(OC_2)H_5)_3\}(OH)_2]$. M. G. Saillard, P. Schützenberger and M. G. Saillard, and G. Quesneville, **platinous toluidine-ethylphosphitedihydroxide,** $[Pt(C_7H_9N)P(OC_2H_5)_3(OH)_2]$; P. Schützenberger, **platinous ethylphosphitedihydroxide,** $[Pt(C_2H_5)_3PO_3(OH)_2]$; and P. Schützenberger and C. Fontaine, **platinous potassium oxyphosphite,** $[Pt(K_3PO_3)O]$, and **platinous sodium oxyphosphite,** $[Pt(Na_3PO_3)O]$.

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§ 18. Intermediate Oxides

According to S. M. Jörgensen,[1] **platinosic oxide,** or **platinum tritatetroxide,** Pt_3O_4, is obtained by heating 1 part of anhydrous sodium chloroplatinite with 4 parts of dry sodium carbonate, until the mixture begins to fuse. The chloroplatinites of potassium and ammonium cannot be substituted for the sodium salt. The black residue which remains after treating the fused mass with water, and with dil. nitric acid, is repeatedly washed by decantation with hot nitric acid, and finally with water acidified with nitric acid, and is then dried at 110°. This oxide is converted into platinum black by formic acid; it is not attacked by mineral acids, not even by boiling aqua regia. It slowly loses oxygen at a red-heat, but it is rapidly reduced in an atm. of hydrogen or coal-gas, even at the ordinary temp. L. Wöhler's observations with this product showed that it is a mixture of platinum monoxide and dioxide, which may by chance approximate to the composition of the assumed Pt_3O_4. According to E. Prost, the *enneahydrate*, $Pt_3O_4.9H_2O$, is formed as an intermediate stage in the hydrolysis of a soln. of the nitrate, $Pt(NO_3)_2.3PtO_2.5H_2O$, which when treated with water yields yellow $PtO_2.3H_2O$; and the filtrate with more water yields $Pt_3O_4.9H_2O$. Boiling water converts the original salt into $Pt_5O_{11}.11H_2O$, which is considered to be a mixture

of hydrates, as L. Wöhler also showed this to be the case with the alleged hydrated platinosic oxide.

According to W. L. Dudley,[2] when spongy platinum is fused with sodium dioxide, and the product washed with water, a yellow substance is obtained which it is supposed to be a sodium salt of platinum sesquioxide, $Pt_2O_3.2Na_2O$; when the alkali of this salt is neutralized with acid, and the product washed. there remains **platinum sesquioxide** or **platinum hemitrioxide,** $Pt_2O_3.2H_2O$. When this *dihydrate* is heated to 100°, it loses no water; at 385°, it loses 5·22 per cent. of water; and at 450°, it forms a dark brown, amorphous powder of the anhydride, Pt_2O_3. J. J. Berzelius supposed that this oxide is formed when powdered platinum is heated with a mixture of potassium nitrate and hydroxide. W. L. Dudley represented the formation of the compound by $2Pt+3Na_2O_2=Pt_2O_3.2Na_2O+Na_2O$; followed by $Pt_2O_3.2Na_2O+4CH_3COOH=Pt_2O_3.2H_2O+4NaC_2H_3O_2$, or else $Pt_2O_3.2Na_2O+4H_2O=Pt_2O_3.2H_2O+4NaOH$. M. Blondel obtained the dihydrate, by heating the trihydrate to 100° to 105°. L. Wöhler found that the product always retains about 2 per cent. of Na_2O very tenaciously, and it behaves like a mixture of sodium platinate and platinic hydroxide. W. L. Dudley observed that the dihydrate is reduced to platinum black by boiling sodium hydroxide and alcohol; it is insoluble in nitric acid, sulphuric acid, and cold, dil. hydrochloric acid, but it is dissolved by hot, conc. hydrochloric acid, in the presence of air, with the formation of platinic chloride.

M. Blondel prepared the *trihydrate*, $Pt_2O_3.3H_2O$, by adding an excess of alkali-lye to a soln. of platinisulphuric acid, $Pt_2(OH)_6.(SO_3)_4(OH)_2.8\frac{1}{2}H_2O$, and drying the well-washed product in vacuo. The brown trihydrate loses a mol. of water at 100° to 105°. It dissolves readily in hydrochloric acid to form a mixed soln. of platinous and platinic chlorides; and it also dissolves slowly in sulphuric acid. M. Delépine prepared the *pentahydrate*, $Pt_2O_3.5H_2O$, as an ochre-yellow insoluble powder, by the prolonged action of cold water on the potassium salt of platinum sulphuric acid, $Pt(OH)(HSO_4)(KSO_4)$. The product retains some alkali, and sulphate very tenaciously.

L. Wöhler and W. Frey obtained the hydrated hemitrioxide, $Pt_2O_3.nH_2O$, by treating a soln. of $Pt_2O_3.3SO_3.H_2SO_4.11{\cdot}5H_2O$ with $2N$-NaOH, and boiling the precipitate with a soln. of sodium carbonate, then washing it with sulphuric acid, followed by water, and drying the product in vacuo. F. Martin, and L. Wöhler and F. Martin prepared a hydrate, $Pt_2O_3.nH_2O$, by adding solid platinum trichloride to a hot soln. of sodium carbonate, or by dissolving the chloride in a 1 : 1-soln. of potassium hydroxide, and precipitating with acetic acid. The hydrate cannot be prepared by oxidizing platinous hydroxide. The brown hydrate is darker in tint if it be precipitated hot. It is not oxidized by boiling with water through which oxygen is passed. It decomposes when dehydrated in vacuo, so that it is doubtful if the anhydrous oxide, Pt_2O_3, has been prepared. The hydroxide dissolves in conc. alkali-lye, and in conc. sulphuric acid. Chemically, it behaves like an oxide in an intermediate position between platinous and platinic hydroxides.

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§ 19. The Higher Oxides of Platinum

Anhydrous **platinum dioxide**, or **platinic oxide**, PtO_2, was obtained by J. J. Berzelius[1] by gently heating the hydrate—E. von Meyer recommended a protracted heating at 175°, and O. Brunck, at 150°. L. Wöhler added that a complete dehydration without some decomposition is not possible. P. Laffitte and P. Grandadam, and A. Baroni obtained the oxide by heating the metals in oxygen at a high press.—*vide* platinous oxide. J. J. Berzelius' dioxide obtained by heating the commercial nitrate for 35 days at 250° to 280°, according to L. Wöhler, contained 13·82 per cent. of oxygen when the theoretical amount is 14·1 per cent. R. Adams and co-workers, W. F. Short, W. F. Bruce, and V. Voorhees and R. Adams prepared it by fusing chloroplatinic acid with sodium nitrate at 500° to 550°, and washing the product with water to eliminate the nitrates. It is used as a catalyst in organic syntheses, and it can be reactivated by shaking it with air or oxygen, but there is an accumulation of poison in use which necessitates its purification. E. P. Schoch obtained the dioxide by anodic oxidation. J. Piazza obtained a mixture of platinum and its dioxide at the platinum cathode during an electric discharge in oxygen; and P. Grandadam, by heating the metal in oxygen under press.

G. P. Thomson and co-workers obtained X-radiograms of the dioxide. The black powder, said J. J. Berzelius, loses oxygen when heated. L. Wöhler said that the oxide is completely decomposed into platinum and oxygen at 450° in an atm. of carbon monoxide; at 510° in an atm. of oxygen; and above 300° in an atm. of carbon dioxide. C. Marie also noted that the salt is decomposed at a dull red-heat. L. Wöhler said that the speed of dissociation depends on the proportion of water of hydration. The last traces of oxygen are very difficult to remove by a blast-flame; in air or carbon dioxide the oxygen is not all expelled in a combustion furnace, but it can be removed by heating in hydrogen. According to L. Wöhler and W. Frey, when platinum dioxide is heated at 510° to 515°, in vacuo, until its oxygen-content diminished below that required for the monoxide, the residue contained metallic platinum; and an examination of the residue indicated that when platinum dioxide is heated, it dissociates into the metal and a solid soln. of either the monoxide or sesquioxide in the dioxide. The equilibrium press. are attained too slowly for measurement. The oxides may be heated for days between 100° and 200° above the temp. corresponding with equilibrium without losing oxygen perceptibly. The metal takes up oxygen equally slowly. The dissociation press. of the monoxide and sesquioxide are, however, higher than that of the dioxide. The evolution of oxygen from the dioxide at constant temp. begins slowly, then becomes very rapid, and finally diminishes gradually. The rapid evolution begins at 514° to 520° when the oxygen content of the oxide has fallen to 11·6 to 12 per cent. It is probable that a supersaturated solution of monoxide or sesquioxide in the dioxide is first formed, and when this has reached a certain concentration it decomposes suddenly. The subject was studied by F. Becker. E. von Meyer observed that hydrogen reduces it energetically, and that it oxidizes hydrogen at ordinary temp. L. Wöhler showed that the dioxide oxidizes hydriodic acid; it is insoluble in dil. and conc. hydrochloric acid, and in sulphuric acid; and it is reduced to the monoxide by sulphurous acid, heated on a water-bath, and the product slowly passes into soln. J. Landauer found that sodium thiosulphate colours the dry dioxide black. L. Wöhler observed that the oxide is insoluble in nitric acid, and in aqua regia; and it is not reduced by arsenic trioxide. E. von Meyer said that it oxidizes carbon monoxide at ordinary temp.; and L. Wöhler, that it is not reduced by ether. A soln. of stannous chloride in hydrochloric acid, on a water-bath, slowly reduces the dioxide to the monoxide.

According to L. Schaffner, pure hydrated platinum dioxide cannot be prepared since the product always contains complex salts—presumably adsorption products. N. W. Fischer said that a hydrate is precipitated by magnesium from a soln. of

platinic chloride; C. Marie, that the hydrate is formed by the action of oxidizing agents—acid soln. of potassium permanganate, dichromate, chlorate, or ferrocyanide—on platinum; L. Wöhler, by heating platinic nitrate to constant weight at 380°, boiling the product with conc. nitric acid, and drying it at 380° to constant weight; L. Wöhler and W. Frey, by boiling conc. soln. of platinic chloride and sodium carbonate; A. Rosenheim, by boiling a soln. of platinic chloride supersaturated with sodium hydroxide; and the replacement of the chlorine in hydrochloroplatinic acid, H_2PtCl_6, by OH-groups by treatment with alkali hydroxide was studied by W. Hittorf, and F. Kohlrausch. L. Wöhler boiled platinic chloride with an excess of $2N$-NaOH, and neutralized the cold soln. with acetic acid when the hydroxide $H_2Pt(OH)_6$ is precipitated as a yellow powder, which, when heated, turns brown and then black. When the precipitated hydroxide is boiled for a long time, it is converted into the compound $PtO_2.3H_2O$, which, when left over sulphuric acid in a desiccator, is converted into the compound $PtO_2.2H_2O$. The latter hydroxide, when heated at 100°, becomes dark coloured, with the formation of the compound $PtO_2.H_2O$, which parts with its water with great difficulty. The monohydrate is insoluble in aqua regia and in hydrochloric acid.

M. Blondel, and H. Töpsöe found that the tetrahydrate loses 2 mols. of water slowly at 100° and becomes yellowish-brown; at 120°, another mol. of water is given off; and at 150°, it darkens in colour owing to reduction. These results do not agree with the observations of L. Wöhler, who found that when the white hydrate precipitated from a cold soln. is dried in air, it is coloured straw-yellow or nankeen-yellow, and it contains 4 mols. of water; if precipitated from boiling soln., the product is ochre-yellow, and it contains 3 mols. of water, and the same results are obtained if the product is dried a short time over calcium chloride; if dried for a long time over conc. sulphuric acid, or a short time on a water-bath, the product is rose-yellow or amber-brown, and contains 2 mols. of water; and if dried for a long time at 100°, the colour is dark brown or deep black, and it contains 1 mol. of water. The last mol. of water is difficult to remove, for after 10 days at 180°, the product contained 6·3 per cent. of water; after 8 days at 250°, 4·6 per cent.; after 24 hrs. at 410° to 450°, 3 per cent.; after heating in oxygen at 400°, 2·6 per cent.; and it decomposes into its elements when heated in oxygen above 510°. F. Becker was unable to dehydrate the hydrated dioxide without some decomposition. C. Marie also noted that the oxide is decomposed at a dull red-heat.

As just indicated, L. Wöhler obtained the *monohydrate*, $PtO_2.H_2O$, from a higher hydrate; and E. von Meyer, by evaporating a mixed soln. of platinic chloride and an excess of sodium carbonate, to dryness, washing the residue with hot water, digesting the solid with dil. acetic acid, and then washing with hot water. The product is black. M. Blondel reported the polymer, $(PtO_2.H_2O)_5$, to be formed by the action of boiling water for 14 days on $(PtO_2)_5.2HCl.9H_2O$, and drying the product at 100° to 105°. E. von Meyer reported the *hemitrihydrate*, $PtO_2.1\frac{1}{2}H_2O$, to be formed by drying at 110° the product of the action of sodium carbonate on platinic chloride. H. Töpsöe prepared the *dihydrate*, $PtO_2.2H_2O$, by heating the higher hydrate at 100°, and it was obtained by L. Wöhler by drying the higher hydrate for a long time over conc. sulphuric acid. J. J. Berzelius observed that alkalies precipitate basic double salts from soln. of most platinic salts, but with platinic nitrate and potash-lye, the hydrate is first precipitated, and, after that, the double salt. L. Pigeon heated a mixture of platinic chloride and sodium hydroxide in a sealed tube for many hours at 180°, and after washing the precipitate with water, dried it in vacuo at ordinary temp. H. Töpsöe evaporated a soln. of platinic chloride mixed with an excess of sodium carbonate to dryness on a water-bath, washed the product with water, then with acetic acid, and finally with hot water. G. C. Wittstein obtained the dihydrate by adding calcium carbonate to a soln. of platinic sulphate, and washing the excess of calcium carbonate from the precipitate by acetic acid, and the calcium sulphate, by water. J. W. Döbereiner obtained the dihydrate by dissolving the alkali from sodium

platinate by means of acetic acid. M. Blondel obtained the polymer, which he called *metaplatinic acid*, $(PtO_2.H_2O)_5$, by the action of mineral acids on the salt $Na_2O.5PtO_2.9H_2O$, and he found it to be sparingly soluble in dil. hydrochloric acid. The dihydrate varies in colour from rust-yellow to amber-brown, and, according to L. Pigeon, the particles are crystalline and polarize light. L. Wöhler obtained the *trihydrate*, $PtO_2.3H_2O$, from the higher hydrate as a precipitate from boiling soln.; E. Prost, by adding water to a soln. of platinic nitrate; but L. Wöhler always found the product to contain some basic nitrate, as was also the case with the anodic deposit obtained in the electrolysis of a soln. of platinic nitrate in nitric acid. The colour of the trihydrate ranges from ochre-yellow to nankeen-yellow. E. Frémy obtained the *tetrahydrate*, $PtO_2.4H_2O$, by boiling a soln. of platinic chloride for a long time with an excess of sodium hydroxide, and precipitating the hydrate with acetic acid. L. Wöhler, and I. Bellucci employed a similar process. I. Bellucci dissolved the dihydrate in molten potassium or sodium hydroxide, and neutralized the product with acetic acid; and he also neutralized a soln. of the alkali salts—$K_2Pt(OH)_6$, or $Na_2Pt(OH)_6$—with acetic acid. M. Blondel treated $Pt(OH)_4.2HCl.nH_2O$ with water in a dialyzer. The colour of the tetrahydrate is white.

L. Wöhler observed that hydrogen does not reduce the monohydrate perceptibly at ordinary temp., but when feebly warmed the reduction proceeds vigorously, and if some platinous oxide is present, such as occurs if the hydrate has been preheated to 400°, the reduction proceeds rapidly at ordinary temp., until it is retarded by the protective action of the platinum formed on the surfaces of the grains. The hydrates lower than the dihydrate make electrolytic gas explode, but the trihydrate only glows in the gas. The decomposition of hydrogen dioxide proceeds slowly in the presence of the hydrated dioxide, and this even in acidic or alkaline boiling soln. when stirred. The freshly-precipitated hydrate was found by W. H. Wahl, C. Marie, and L. Wöhler to be soluble in conc. hydrochloric acid, but after being dried on a water-bath, it is no longer completely soluble. L. Wöhler observed that dissolution occurs immediately if the hydrate has been reduced with stannic chloride, or with sulphurous acid. W. Bersch observed that the dihydrate produces an alkaline reaction with a soln. of potassium iodide, but it has no perceptible action on soln. of potassium chloride or bromide. W. H. Wahl found that the freshly-precipitated hydrate is soluble in sulphuric acid, and L. Wöhler added that if the hydrate has been dried on a water-bath, dissolution is incomplete. C. Marie said that the hydrate is not perceptibly soluble in dil. sulphuric acid—except in the presence of reducing agents like sulphurous acid or alcohol. If the hydrated dioxide be heated with conc. sulphuric acid, it loses water, and darkens in colour. For the compound with ammonia, *vide infra*, fulminating platinum. W. H. Wahl observed that the freshly-precipitated hydrate is soluble in nitric acid, but L. Wöhler added that after the hydrate has been dried on a water-bath, it becomes insoluble in that acid. W. H. Wahl observed that a dil. aq. soln. of phosphoric acid dissolves a small proportion of the hydrated dioxide in the cold, and much more when heated; the solubility also increases as the conc. of the acid is increased. The hydrated dioxide is soluble in formic acid, and very sparingly soluble in acetic acid. Boiling acetic acid gradually decomposes the hydrated dioxide. J. W. Döbereiner, E. Frémy, and H. Töpsöe said that different reports as to the solvent action of acetic acid are based on differences in the degree of hydration of the specimen under observation. The best solvent for the hydrated dioxide was found by W. H. Wahl to be oxalic acid. Dissolution takes place rapidly even in the cold, and when aided by heat platinic oxalate is formed, and some carbon dioxide is evolved owing to the decomposition of the acid. L. Wöhler also found that if boiled for 4 hrs. with *N*-soln. of oxalic acid, the hydrated dioxide is reduced to metal. W. Bersch observed no reaction with potassium thiocyanate. R. Adams and co-workers, and F. D. Aguirreche discussed the use of platinic oxide as a catalyst in organic hydrogenations, etc. Dil. aq. soln. of sodium hydroxide,

and, better still, potassium hydroxide dissolve the hydrate at ordinary temp. L. Wöhler found that the hydrated dioxide accelerates the decomposition of hot soln. of potassium permanganate, and when boiled with a conc. soln. of platinic chloride in the presence of acetic acid, the hydrated dioxide is reduced to metal. H. Kautsky and W. Baumeister studied the adsorption of the $[Pt(OH)_6]''$-ions by thorium hydroxide gel; and A. Rosenheim, the action of platinic hydroxide on tungstates.

B. Gerdes prepared **platinic hexamminohydroxide,** $[Pt(NH_3)_6(OH)_4]$, by boiling the chloride with an eq. quantity of silver oxide, and cooling the filtered liquid. The white hexagonal plates are sparingly soluble in water; the soln. has an alkaline reaction; it decomposes ammonium salts; absorbs carbon dioxide from the air to form a carbonate; and forms salts with acids.

C. Gerhardt prepared **platinic tetrahydroxydiammine,** $[Pt(NH_3)_2(OH)_4]$, by the action of ammonia on a boiling soln. of the corresponding nitrate, cooling the liquid, washing the precipitate, and drying at 130°. The yellow, microcrystalline powder is not changed at 130°; it decrepitates at a higher temp. losing water and ammonia, and leaving platinum behind. It is scarcely soluble in water, but soluble in hot, dil. acids; boiling potash-lye does not dissolve or decompose the compound. It was studied by W. Odling, C. Weltzien, H. Kolbe, C. Grimm, and P. T. Cleve. B. E. Dixon prepared **silver platinic hydroxytriamidodiamminohydroxide,** $[Ag_3\{Pt(NH_3)_2(NH_2)_3(OH)\}_2](OH)_3$.

J. Jacobsen prepared **platinic decahydroxyammine,** $[NH_3Pt(OH)_5]_2$, by pouring an excess of ammonia into a soln. of dichloroplatinic acid. The liquid turns a dark colour, and finally precipitates a brown, flocculent mass containing no chlorine and resembling ferric hydroxide. Washed with boiling water until free from ammonia and dried, this precipitate presents a conchoidal structure. If dried at 100° and then over sulphuric acid, it rehydrates with such avidity that the particles jump about. When it is heated gently above 250°, the compound blackens, and finally explodes with some violence, giving spongy platinum, nitrogen, oxygen, and water vapour. If pyridine is employed in place of ammonia, a similar detonating compound is formed, namely, **platinic decahydroxypyridine,** $C_5H_5N[Pt(OH)_5]_2$. The fulminating compound is easily soluble in hydrochloric acid, and its composition corresponds with $\{Pt(OH)_5\}_2(NH_3)$, it loses water when heated at 220°, 6 mols. being removed.

The dihydrate $PtO_2.2H_2O$ can be formulated as the tetrahydroxide, $Pt(OH)_4$, and M. Blondel added that since two of the hydroxyl groups are basic, and two acidic, the dihydrate can be regarded as a **dihydroxyplatinic acid,** $H_2PtO_2(OH)_2$, forming in the one case potassium platinate, $K_2PtO_2(OH)_2.2H_2O$, and in the other case $H_2PtO_2(SO_4).3H_2O$. This subject was discussed by I. Bellucci, and H. Töpsöe. I. Bellucci regarded the tetrahydrate as a **hexahydroxyplatinic acid,** $H_2Pt(OH)_6$, in which the six chlorine atoms of hydrochloroplatinic acid, H_2PtCl_6, have been replaced by six hydroxyl-groups. M. Blondel said that before drying, the tetrahydrate contains the group $Pt(OH)_4$, and after drying it is not to be regarded as $Pt(OH)_4.2H_2O$, but rather as $H_2Pt(OH)_6$. S. W. Pennycuik observed the acid in soln. of colloidal platinum.

W. J. Pope and S. J. Peachey prepared **trimethyl platinic hydroxide,** $(CH_3)_3Pt(OH)$, by boiling an acetone soln. of the iodide with silver hydroxide.

Several observers have noted the formation of **potassium platinates,** thus, H. Davy,[2] and K. A. Hofmann and H. Hiendlmaier found that the yellow powder obtained by the combustion of a platinum-potassium alloy behaved like a platinate; and S. Tennant obtained by the action of fused potassium nitrate—(i) a brown insoluble product containing a small proportion of potassium oxide, and (ii) a brown soluble product. J. J. Berzelius added that when potassium nitrate and hydroxide are fused with platinum, and the product washed with water, there remains a partly purple, and partly yellow oxide which dissolves with difficulty in hydrochloric acid leaving a residue of platinum. When potassium chloroplatinate is boiled with

an excess of potash-lye, there is formed a yellow liquid which dries to a scarlet mass. When this product is heated not quite to redness, and the excess of potassium hydroxide and chloride are washed out, there remains a rust-yellow, colloidal platinate which is coagulated by the addition of a salt. It contains 7 per cent. of potassium oxide; hydrochloric acid, and hot sulphuric and nitric acids remove the alkali; conc. hydrochloric acid slowly converts it into potassium chloroplatinate, and platinic chloride; at a red-heat, the platinate passes into platinite by the loss of oxygen; it detonates violently when heated with combustible matters.

M. Blondel dissolved freshly-precipitated, hydrated platinum dioxide in conc. potash-lye, evaporated the decanted liquor over sulphuric acid, and dried the yellow crust in air and then in vacuo. The composition agreed with that of **potassium platinate,** $K_2PtO_3.3H_2O$. When an acid is added to the aq. soln. of potassium platinate it precipitates hydrated platinum dioxide. The soln. is stable when concentrated and in the presence of an excess of alkali-lye. When dried at 110°, potassium platinate passes into **potassium hexahydroxyplatinate,** $K_2Pt(OH)_6$. I. Bellucci and N. Parravano reported that the golden yellow crystals, obtained by seeding the aq. soln. with the corresponding stannic salt, are trigonal, with the axial ratio $a:c=1:1{\cdot}9952$, and $\alpha=69°\ 11'\ 14''$. The (111)-cleavage is good; and the double refraction is positive. The salt loses 0·30 per cent. of water at 160°; 0·37 per cent., at 200°. P. Niggli and W. Nowacki, and H. Seifert studied the crystals. According to I. Bellucci, decomposition begins about 160°, and at a higher temp. the salt decomposes into potassium hydroxide and platinum. The salt forms a very alkaline soln. with water, and the electrical conductivity of a soln. containing an eq. of the salt, $\frac{1}{2}K_2Pt(OH)_6$, in v litres of water at 25°, is:

v . . .	32	64	128	256	512	1024
λ . . .	93·7	97·6	102·1	105·5	109·6	113·6—λ_∞=117·4

The transport number of the anion $Pt(OH)_6$ is 43·1. Acetic acid precipitates $H_2Pt(OH)_6$ from the aq. soln.; and silver and thallium nitrates precipitate the corresponding salts. The salt is insoluble in alcohol. M. Blondel, and I. Bellucci prepared **sodium hexahydroxyplatinate,** $Na_2Pt(OH)_6$, in a similar manner. When the clear, alkaline soln. is kept a few days it becomes colloidal, and precipitates $Na_2O.3PtO_2.6H_2O$; and if the soln. is dialyzed, it forms a soln. which on evaporation yields insoluble sodium pentaplatinate. I. Bellucci prepared **silver hexahydroxyplatinate,** $Ag_2Pt(OH)_6$, by adding an excess of a soln. of silver nitrate to a soln. of the potassium salt, washing the precipitate by decantation, and drying it on a porous tile; at 100°, the pale yellowish-white powder becomes superficially brown when exposed to light for a long time. It is insoluble in water; acetic acid precipitates $H_2Pt(OH)_6$ from the aq. soln. The aq. soln. can be washed without decomposition. I. Bellucci also prepared **thallous hexahydroxyplatinate,** $Tl_2Pt(OH)_6$, by the method employed for the silver salt.

G. Rousseau prepared two **sodium platinates** with $Na_2O:PtO_2:H_2O=$ 2·33 : 87·02 : 10·65, and 5·34 : 86·69 : 7·97. He said: amorphous sodium platinate, formed by the action of platinic chloride on sodium hydroxide, does not crystallize even at a temp. sufficient to volatilize the excess of alkali. The crystallized salt can, however, readily be obtained by heating a mixture of equal parts of sodium hydroxide and chloride in a platinum crucible at the m.p. of copper for 2 hrs. In order to avoid the destruction of the crucible, it is advisable to add finely-divided platinum to the mixture. If the platinate which forms is continually stirred into the molten mass, it separates in brownish-yellow, microscopic lamellæ, which have a feeble action on polarized light and dissolve readily in hydrochloric acid. If, however, the platinate is allowed to collect in a ring at the surface of the fused mass, it forms much larger reddish-brown hexagonal lamellæ, which dissolve with difficulty in hydrochloric acid. These platinates become anhydrous at 200° to 300°, and at a dull-red heat decompose with separation of

metallic platinum and sodium hydroxide. The stability of the platinates is of the same order as that of the manganates and ferrates, and the composition of the latter is almost identical with that of the corresponding platinum compounds.

M. Blondel found that red, insoluble scales of *sodium metaplatinate*, or **sodium pentaplatinate,** $Na_2O.5PtO_2.9H_2O$, are formed when a clear, alkaline soln. of sodium hexahydroxyplatinate is dialyzed for some days, and then evaporated over sulphuric acid, and dried in vacuo. M. Blondel also found that if the clear, alkaline soln. of the hexahydroxyplatinate is kept for some days, it becomes colloidal, and then deposits reddish-yellow, pulverulent **sodium triplatinate,** $Na_2O.3PtO_2.6H_2O$. H. G. Söderbaum obtained the same salt by melting sodium chloroplatinate with an equal weight of sodium hydroxide, extracting the cold mass with water, neutralizing the liquid with dil. hydrochloric acid to precipitate the platinate, washing the product by suction, and drying it by pressure between filter-paper; and J. W. Döbereiner exposed a clear mixed soln. of sodium carbonate and hydrochloroplatinic acid to sunlight for some days, or heated the mixed soln. to 100°, and obtained a reddish-yellow, pulverulent, partly crystalline precipitate of the triplatinate. If the soln. of the two salts are used in as concentrated a state as possible, the mixture boiled down to dryness, and the residue washed with water, a denser precipitate is obtained, having more of an ochre-yellow colour. J. W. Döbereiner said that at a red-heat the salt first gives off water, afterwards oxygen gas, and leaves a black residue, from which the soda may be dissolved out by water. The residual black powder appears to be a mixture of platinum and platinic oxide, since hydrochloric acid extracts platinic oxide. Formic acid, with the aid of heat, converts sodium platinate into platinum black, causing at the same time a brisk evolution of carbon dioxide and formation of sodium formate. Heated aq. soln. of oxalic acid dissolve sodium platinate with evolution of carbon dioxide, forming a dark liquid, which, on cooling, first becomes green and then dark blue, and deposits copper-coloured needles of platinous oxalate. Acetic acid withdraws all the soda from sodium platinate together with a small quantity of platinic oxide, and leaves ochre-yellow hydrated platinic oxide. Dil. nitric acid dissolves it easily and completely, forming a deep yellow liquid, which forms, with nitrate of silver, a yellow precipitate, soluble in nitric acid. Dil. oxygen-acids extract the soda without dissolving the platinic oxide; from the denser ochre-yellow compound, strong nitric acid dissolves out nothing but soda.

Platinum is attacked by the alkaline earth oxides—by calcium oxide least, and by barium oxide most; platinum crucibles are attacked by fused barium nitrate. J. J. Berzelius mixed a soln. of a platinic salt with a large excess of baryta and obtained **barium platinate** as a light yellow powder which at a red-heat gives a mixture of baryta and platinum. G. Rousseau observed that when barium oxide, mixed with an equal quantity of the chloride or bromide, is heated for several hours at 1100° in an open platinum crucible, a considerable quantity of crystallized barium platinate is formed. It has the composition $3BaO.PtO_2$, and is more readily obtained in crystals by first producing the amorphous platinate by heating platinic chloride with barium oxide, and then adding a sufficient quantity of barium chloride or bromide and heating at the melting point of copper. The alkalinity of the mixture has great influence on the crystallization. The crystals are prisms with hexagonal bases, and are insoluble in acetic acid, but dissolve in hydrochloric acid. At an orange-red heat, in presence of barium chloride, the platinate decomposes and metallic platinum separates. If the proportion of barium oxide employed is less than 30 per cent., the product is barium platinate, $BaPtO_3$. H. Töpsöe obtained the *tetrahydrate*, $BaPtO_3.4H_2O$, by boiling a mixture of a soln. of hydrochloroplatinic acid and barium hydroxide. The precipitate contains some chloride. Dil. soln. furnish yellowish-white scales, and conc. soln., straw-yellow, microscopic, plumose or stellar crystal aggregates. The salt is not changed at 100°, but at 300° to 400° it forms the dark brown *monohydrate*, $BaPtO_3.H_2O$, which is insoluble in dil. nitric acid. The tetrahydrate is sparingly soluble in water,

baryta water, or soda-lye; it is soluble in acids, but cold acetic acid has no action, whilst the hot acid forms barium acetate and hydrated platinum dioxide.

For the *tin platinates*, *vide* **7.** 46, 14; the *vanadium platinates*, **9.** 54, 6; *chromium platinates*, **11.** 60, 15 and 16; the *molybdenum platinates*, **11.** 61, 11; and the *tungsten platinates*, **11.** 62, 12.

According to E. Prost,[3] an oxide, $Pt_5O_{11}.11H_2O$, is obtained by boiling a soln. of hydrated platinum dioxide in conc. nitric acid. L. Wöhler could not prepare this product, and considered it to be a mixture of different hydrated oxides.

L. Wöhler[4] and co-workers, C. Marie, M. le Blanc, and R. Ruer showed that the oxide film which was observed by F. Kohlrausch to form on the anode during the electrolysis of a soln. of platinic chloride is possibly **platinum trioxide,** PtO_3; and that the same film is formed when the metal becomes passive. F. Haber and S. Grinberg showed that it liberates iodine from potassium iodide. According to L. Wöhler and F. Martin, when the yellow soln. of hydrated platinum dioxide in $2N$-KOH is oxidized anodically whilst the soln. is well-cooled, the anode soon becomes covered with a golden yellow, amorphous deposit, which peels off in thin, silky plates. It is **potassium platinic decoxide,** $K_2O.3PtO_3$. The trioxide can be obtained from this salt by treatment with ice-cold $0{\cdot}5N$-acetic acid. The reddish-brown product contained slightly less oxygen than that necessary for the trioxide, owing to the fact that it readily parts with some of its oxygen as soon as all the alkali has been removed. On keeping, the percentage of oxygen gradually decreases, but it never falls to that necessary for the dioxide, probably because a solid solution of the trioxide in the dioxide is formed. Platinum trioxide is not acted on by dil. sulphuric, nitric, or acetic acids. It slowly liberates chlorine from dil. hydrochloric acid. Sulphurous acid dissolves it with the formation of a colourless complex. Conc. sulphuric and nitric acids slowly decomposed it with the formation of the dioxide. On gently heating, it gives the dioxide. In the cold it has no action on alcohol or acetic acid. The oxidation which takes place on warming is due to the dioxide which is formed. It does not decompose into hydrogen dioxide, and must therefore be classed as a polyoxide or peroxide of platinum of the constitution

$$\mathrm{O{=}Pt}\genfrac{}{}{0pt}{}{\diagup\!\!\diagup \mathrm{O}}{\diagdown\!\!\diagdown \mathrm{O}}$$

G. Grube,[5] in his study of the behaviour of the oxygen electrode, found that potentials from 1·5 volts downwards are due to solid soln. of platinum trioxide in platinum dioxide, or of platinum dioxide in platinum monoxide. Since, however, platinum electrodes can be polarized up to potentials of 2 volts, G. Grube suggested that an unknown **platinum tetroxide,** PtO_4, is formed.

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§ 20. Platinum Fluorides

H. Moissan [1] found that fluorine free from hydrogen fluoride does not attack platinum below 100°, and combination does not readily occur below 500° to 600°. If hydrogen fluoride is present, the reaction occurs more readily even in the case of liquid hydrogen fluoride saturated with fluorine. He prepared **platinum difluoride,** or **platinous fluoride,** PtF_2, together with the tetrafluoride, by heating platinum wire to 500° or 600° in a current of fluorine. C. Poulenc observed that some difluoride is formed when ammonium fluoplatinate is heated over 300°. According to H. Moissan, the tetrafluoride is soluble in water, but the difluoride remains attached to the surface of the metal as an insoluble, green layer. On ignition, it decomposes into fluorine and platinum. H. Moissan prepared **platinous phosphopentafluoride.**

J. J. Berzelius reported that when an aq. soln. of potassium fluoride is added to an aq. soln. of platinic chloride, free from an excess of acid, as long as a precipitate continues to form, and the filtered liquid evaporated, platinic fluoride may be extracted from the mass by means of alcohol—potassium chloroplatinate remains. The alcoholic liquid mixed with water is then evaporated. On cooling to a low temp., a non-crystalline, yellow, transparent mass is formed which is completely soluble; and if a temp. of 60° be employed, the mass becomes dark brown, and

when extracted with water leaves a basic salt undissolved. S. G. Hedin reported the possible existence of **platinous difluorobispyridine,** $[Pt(C_5H_5N)_2F_2]$.

C. Poulenc observed that **platinum tetrafluoride** or **platinic fluoride,** PtF_4, cannot be obtained by heating platinum tetrachloride in hydrogen fluoride; since, according to W. Jeroch, and O. Ruff and W. Jeroch, only dark brown, anhydrous platinic chloride is formed below 200°, and over 220°, the platinic chloride decomposes into its constituent elements. Nor was platinum tetrafluoride obtained by heating platinum tetrachloride with molten potassium hydrofluoride at 280°. H. Moissan prepared the tetrafluoride by heating a bundle of platinum wire to dull redness in a platinum or fluorspar tube through which a current of fluorine is passed. As soon as combination is complete, the product is transferred to a dry tube. G. Gore observed that some of this salt is formed when silver fluoride is melted with iodine in a platinum vessel; and O. Ruff and J. Zedner, when fluorine is passed over columbium in a platinum vessel.

Platinum tetrafluoride furnishes a deep red, fused mass, or chamois-yellow crystals resembling those of anhydrous platinum tetrachloride. The salt is extremely hygroscopic, and cannot be kept for a long time in a dried but corked tube. It decomposes at a red-heat, forming crystals of platinum; and when heated in a glass vessel, the glass is energetically decomposed to form platinum and silicon tetrafluoride. When treated with a small proportion of water, a tawny coloration is first produced, then heat is rapidly developed, and the salt is decomposed with the formation of hydrofluoric acid and hydrated platinum dioxide. Very dil. soln. are more stable, but they behave similarly if the liquid is warmed. This hydrolysis shows why platinic fluoride cannot be prepared by the action of hydrofluoric acid on hydrated platinum dioxide; and renders it questionable if J. J. Berzelius' preparation was what it was thought to be. The fact that fluorine containing hydrogen fluoride attacks platinum more vigorously than fluorine alone; and the existence of double salts with the alkali metals made H. Moissan suggest that possibly a platinic hydrofluoride, $PtF_4.nHF$, can be formed. Platinic fluoride forms crystalline compounds with the fluorides and chlorides of phosphorus and boron.

J. J. Berzelius obtained a dark brown, gummy mass from a mixture of his platinum fluoride and ammonium fluoride. The product was resolved by water into a soluble acidic salt, and an insoluble basic salt. It was insoluble in alcohol. According to C. Poulenc, there is a state of equilibrium between ammonium fluoride and platinic chloride in the molten state, some **ammonium fluoplatinate,** probably $(NH_4)_2PtF_6$, is formed, but it cannot be separated from the chloroplatinate which is associated with it. C. Poulenc obtained it by the action of ammonium fluoride on hydrated platinum dioxide, and the compound is not decomposed when heated to 300° in a current of hydrogen fluoride, but it is decomposed at a higher temp. to form platinum, platinum tetrafluoride, etc.

J. J. Berzelius obtained **potassium fluoplatinate,** K_2PtF_6, by treating a soln. of potassium fluoride with less than an eq. quantity of hydrochloroplatinic acid, decanting the liquid from the precipitated potassium chloroplatinate, and evaporating. The dark brown, deliquescent salt is insoluble in alcohol. H. I. Schlessinger and M. W. Tapley obtained it by heating finely-divided platinum with the lead salt $3KF.HF.PbF_4$, and they studied the absorption spectra. J. J. Berzelius also reported **sodium fluoplatinate** to be a dark brown, gum-like mass which is hydrolyzed by water into a soluble acidic salt, and an insoluble basic salt.

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§ 21. Platinum Mono-, Di-, and Tri-Chlorides

M. C. Lea [1] said that when potassium chloroplatinate (12 grms.) is heated in a covered vessel, on a water-bath, with potassium hydrosulphite (9 grms.) and water (160 c.c.) for 10 to 12 hrs., the reduction is complete, and a red salt crystallizes out on evaporation. Similar results were obtained by heating potassium chloroplatinite (9 grms.) with potassium hypophosphite (1 grm.) and water (300 c.c.), at 80° to 90°, for 18 to 20 hrs. The completion of the action is shown by the pure ruby colour of the soln., the least shade of orange indicating the presence of chloroplatinite. The first method is the safest, as the reduction cannot go beyond the chloroplatinite, but in the second method, the red salt separates more easily and completely, and, with care, very good results are obtained. If, when reducing with potassium hypophosphite, the action is continued after complete conversion into the red salt, the solution rapidly changes to dark brown. Hydrochloric acid has no effect on this solution, nitric acid decolorizes it, potash causes a brown precipitate soluble in excess of the precipitant, and ammonia a brown precipitate insoluble in excess. This compound could not be isolated, but M. C. Lea considered it to be **platinum subchloride.** According to S. Streicher,[2] and L. Wöhler and S. Streicher, **platinum monochloride,** PtCl, is formed when brownish-green platinum dichloride is kept between 581° to 583°. This is a very narrow range of stability. It is formed along with platinum, and appears as a pale yellowish-green powder. The strong sublimation of the chloride at 500°, and the simultaneous lowering of the partial press. of the chlorine by admixture with oxygen or carbon dioxide decreases as the tetrachloride passes into dark green trichloride to brownish-green dichloride, and to a mixture of yellowish-green monochloride and metal. The mol. heat of formation is (Pt,Cl)=16·10 Cals. E. Sonstadt said that a *hydrated* monochloride, $PtCl.nH_2O$, is formed when a very dil. soln. of potassium chloroplatinate is exposed to direct sunlight; or by heating a soln. of 1 part of potassium chloroplatinate in 10,000 parts of water for some days. The reaction is represented: $K_2PtCl_6=2KCl+PtCl_4$, followed by $2PtCl_4+6H_2O=2PtCl+6HCl+3H_2O_2$. The free acid present in platinum tetrachloride, when used alone, prevents the reaction. The hydrated salt, when treated on the water-bath with conc. soda-lye, turns brown, and dissolves to a slight extent. But the brown residue is only partly dehydrated, and recovers its original colour after washing and exposure. The soda soln. deposits the unchanged salt on dilution and long exposure to the air. It dissolves readily in hydrochloric acid; slightly in hot dil. sulphuric acid, apparently without decomposition; in moderately dil. nitric acid, used in large proportion, it dissolves to a deep brown liquid, which, evaporated to dryness on the water-bath until no acid odour is perceptible, leaves a dark brown residue. This dissolves in hot water to a clear dark brown liquid, which, on further heating, suddenly deposits the whole of the original salt, less any impurities present, which remain in the soln. The precipitate, when collected on a filter, is deeper coloured than before, being of an orange tint. The filtrate is free from platinum; but on continued washing with water, the salt dissolves slightly, and the filtered liquid becomes clouded. P. C. Ray and co-workers prepared **platinum ethylsulphinomonochloride,** $PtCl.(C_2H_5)_2S$, or $\{(C_2H_5)_2S:PtCl\}_2$; **platinum ethylsulphinobenzylaminomonochloride,** $Pt_2Cl(CH_2.C_6H_5.NH_2)(C_2H_5)_2S$; **platinum ethylsulphinobispyridinomonochloride,** $Pt_2Cl(C_5H_5N)_2(C_2H_5)_2S$; **platinum hemiethylsulphinopyridinomonochloride,** $2Pt_2Cl(C_5H_5N).(C_2H_5)_2S$; and **platinum ethylsulphinoethylaminochloride,** $PtCl(C_2H_5.NH_2).(C_2H_5)_2S$.

P. Schützenberger [3] noted that some **platinum dichloride** or **platinous chloride,** $PtCl_2$, is formed when spongy platinum is heated in dry chlorine at 240° to 250°; there is scarcely any action at 200°; and the yield is no greater at 300°. According to L. Troost and P. Hautefeuille, chlorine attacks platinum at 1400° to form platinum dichloride which can be condensed in a cooled tube before the dichloride has time to decompose. The phenomenon was discussed by P. Duhem. L. Pigeon

heated platinum tetrachloride to 400° in a current of chlorine, and C. Gordon heated hydrated platinum tetrachloride on a sand-bath until the colour changed from dark brown to dark grey. L. Wöhler and F. Martin preferred platinum tetrachloride for this preparation in preference to hydrochloroplatinic acid. J. J. Berzelius recommended evaporating the hydrochloroplatinic acid to dryness, and, with frequent stirring, raising the temp. to about 232°, and, added L. N. Vauquelin, washing out the undecomposed acid with water. G. Magnus employed a similar process, and said that if the heating be insufficient to decompose all the platinum tetrachloride, the residue dissolves completely in water, forming a dark brown, nearly opaque liquid, because the platinum dichloride is rendered soluble through the medium of the tetrachloride. On evaporating the soln. the monochloride is deposited in the form of a brown powder, the quantity being the greater, the more the liquid is concentrated; and on evaporating to dryness and digesting in cold water, the whole of the brown powder remains undissolved. This powder, notwithstanding its different colour, has the same composition as the greenish-grey platinum dichloride, but dissolves much more easily in hydrochloric acid. After the liquid containing the platinum tetrachloride has been decanted off, the brown powder is no longer soluble in water, but dissolves again in the decanted liquid, on the application of heat and the addition of water. K. Seubert observed that the product is contaminated with oxychloride. F. Hoffmann recommended heating the hydrochloroplatinic acid at 340° in a current of carbon dioxide; W. A. Shenstone and C. R. Beck said at 357° in a current of hydrogen chloride; L. F. Nilson recommended 300°; and L. Pigeon, at 357° in a vessel containing potassium hydroxide and in vacuo. K. Seubert dissolved spongy platinum in conc. hydrochloric acid while passing a current of chlorine through the liquid heated on a sand-bath, evaporated the dark brown soln., and heated it to 230° to 240°. F. Gramp obtained yellow crystals of the dichloride by the action of iodine on a soln. of platinum tetrachloride. M. Katayama noted the anodic formation of platinum dichloride in the warm cell Pb : $PbCl_{2 solid}$: Cl(Pt anode).

The colour of these preparations ranges from dark olive-green to greenish-grey or greyish-green; but if the product is contaminated with platinic chloride, W. Peters said that the colour is greyish-brown. The product is pulverulent, but F. Gramp obtained it in yellow crystals. The colour was discussed by W. Ackroyd. V. M. Goldschmidt, and L. Pauling discussed the lattice structure. C. H. D. Bödecker found the sp. gr. to be 5·87; and R. Klement gave 6·054 for the sp. gr. at 25°/4°, and 44·0 for the mol. vol. J. Dewar and A. Scott observed that the vapour density is 251—theoretical for $PtCl_2$, 265·7; and L. Rügheimer and E. Rudolfi found that the mol. wt. of soln. in bismuth chloride ranges from 258·8 to 260·8. J. J. Berzelius observed that the dichloride is decomposed by heat into chlorine and platinum, and F. P. Dunnington, and W. A. Shenstone and C. R. Beck recommended this as a process for preparing chlorine of a high degree of purity. C. Nogareda studied the formation of the chloride from its elements. L. Wöhler and F. Martin said that when the dichloride is heated in chlorine above 400° its weight does not change; and S. Streicher, and L. Wöhler and S. Streicher, that the temp. of formation and decomposition is 582°. No decomposition occurs at 560° although the salt is very volatile. The loss of weight at 560°, 570°, and 580° is approximately the same, but at 590°, the loss is doubled. In a current of chlorine at 581° to 583°, platinum monochloride is formed. The volatility of the salt when heated to decomposition was noted by G. Matthey, and W. A. Shenstone and C. R. Beck added that the properties of the sublimate are not always those of platinous chloride being sometimes a yellowish, fusible substance converted by a strong heat into a red, infusible solid; and it is sometimes this same red, infusible solid. L. Wöhler and F. Martin gave for the thermal value of the reaction $2PtCl+Cl_2=2PtCl_2+32·17$ Cals., and for $2Pt+Cl_2=2PtCl+32·21$ Cals. S. Meyer gave for the magnetic susceptibility $-0·029\times10^{-6}$ mass unit, and A. N. Guthrie

and L. T. Bourland found the susceptibility to be independent of temp. D. M. Bose and H. G. Bhar also studied the magnetic properties.

V. Ipatéeff and A. Andreevsky observed that *hydrogen*, at elevated temp. and press., acting on 3 to 30 per cent. soln. of platinous chloride, precipitates the platinum, and the proportion of platinum precipitated is the greater, the greater is the initial conc. of the soln. The addition of acids, and of ferric chloride inhibits the reaction, but without affecting the influence of the other factors. With 0·01 to 1 per cent. soln., in the presence of iron and nickel salts, the reduction is complicated and slow, particularly if mineral acids are present. W. J. Russell found that hydrogen precipitates the metal from platinum salts at ordinary temp. and press. J. J. Berzelius said that the greenish-grey powder behaves like a fatty substance in that it is scarcely wetted by *water* ; and that the salt is not affected by water ; G. Magnus also noted that the brown powder is insoluble in water, but is soluble in the mother-liquor. E. Knoevenagal and E. Ebler observed that no precipitate is formed with hydrogen dioxide. J. J. Berzelius, and G. Magnus noted that the salt is soluble in hot *hydrochloric acid*, and, with access of air, some hydrochloroplatinic acid is formed—L. F. Nilson added that some hydrochloroplatinic acid may be formed with the separation of platinum—*vide infra*. *Potassium iodide* colours soln. of platinous salts a dark reddish-brown, and after a time the soln. is decolorized as a precipitate of platinous iodide is formed. O. Stelling estimated platinum by the potentiometric titration of platinous salts with a $0{\cdot}1N$-soln. of *potassium bromate*. H. Rose observed that *hydrogen sulphide*, and *ammonium sulphide* give a brown soln. with a hydrochloric acid soln. of platinous chloride, and later platinous sulphide is precipitated, and the precipitate dissolves in a large excess of ammonium sulphide. J. J. Berzelius observed that the dichloride is not changed by *sulphuric acid* or by *nitric acid* ; and that boiling *aqua regia* converts it into hydrochloroplatinic acid. H. Rose observed that *stannous chloride* colours soln. of platinous salts reddish-brown without forming a precipitate. P. Schottländer found that a soln. of ammonium chloroplatinite and *sodium thiosulphate* furnish platinous thiosulphate, as a white precipitate, when treated with alcohol. W. Peters observed that in an atm. of *ammonia*, additive compounds are formed—*vide infra*—M. Delépine noted that an ammine is precipitated when *ammonia* is added to the aq. soln. H. Rose observed no precipitate is formed by addition of a soln. of *sodium phosphate*. G. Gore said that platinous chloride is insoluble in liquid ammonia, and E. Divers, that it is insoluble in an ammonia soln. of ammonium nitrate. P. Schützenberger prepared the compounds with *carbon monoxide* indicated below, and the results were confirmed by W. Manchot. W. Manchot and E. Enk found that at 140°, platinum dichloride and tetrachloride with carbon monoxide form **platinum dicarbonyldichloride,** $PtCl_2(CO)_2$; and W. Manchot and G. Lehmann observed that the carbonyl, $2PtCl_2.3CO$, is also formed. P. Schützenberger and C. Fontaine, and A. Rosenheim and W. Löwenstamm prepared from *phosphorus trichloride* the complex **platinous dichlorobisphosphorotrichloride,** $[Pt(PCl_3)_2Cl_2]$, and **platinous dichlorobisphosphorotrihydroxde,** $[Pt\{P(OH)_3\}_2Cl_2]$; **platinous dichlorophosphorotrihydroxide,** $[Pt\{P(OH)_3\}Cl_2]$, **platinous chlorophosphorotrihydroxidodihydrophosphite,** $[Pt\{P(OH)_3\}Cl(H_2PO_3)]$, and P. Schützenberger, **platinous dichlorosilverphosphite,** $[Pt\{P(OAg)_3\}_2Cl_2]$. P. Schützenberger, P. Schützenberger and C. Fontaine, E. Baudrimont, A. Werner, G. Quesneville, A. Rosenheim and W. Löwenstamm, A. Rosenheim and W. Levy, and D. Cochin described **platinous dichlorophosphorotrichloride,** $[Pt(PCl_3)Cl_2]_2$, and **platinous dichlorophosphorotrichloroplatinite,** $[Pt(PCl_3)Cl_2]_2.PtCl_2$.

H. Rose observed that mercuric cyanide does not react immediately with soln. of platinous chloride ; nor has potassium ferrocyanide or ferricyanide any action. M. S. Kharasch and T. A. Ashford prepared complex salts with *ethylene*. K. A. Hofmann and H. Kirmreuther found that the ethylene halides gradually reduce soln. of platinous chloride. L. Tschugaeff observed that when platinous chloride is heated on a water-bath, the *tertiary amines* precipitate platinum.

E. Beckmann and W. Gabel found that platinous chloride is soluble in *quinoline.* H. Rose found that *oxalic acid* gives no precipitate with soln. of platinous salts. W. Eidmann found that the salt is insoluble in *acetone ;* J. J. Berzelius, that an aq. soln. of *potassium hydroxide* converts it into hydrated platinous oxide and potassium chloride. H. Rose added that *potassium hydroxide* does not act on soln. of platinous salts, and that *potassium* or *sodium carbonate* gives a dark brown precipitate. F. Müller and A. Riefkohl studied the solubility in 2*N*-soln. of *sodium chloride.* L. Rügheimer and E. Rudolfi found that the chloride is soluble in a soln. of *bismuth chloride.* G. Mazzaron found that platinum chloride gives chlorine not chromyl chloride when treated with *potassium dichromate* and sulphuric acid.

Two compounds of platinous chloride with hydrochloric acid have been reported. L. F. Nilson said that **platinous hydrotrichloride,** $PtCl_2.HCl.2H_2O$, is formed by decomposing barium chloroplatinite with the theoretical quantity of sulphuric acid ; evaporating the filtered liquid first at 50°, and then in vacuo ; and drying the product over sulphuric acid and potassium hydroxide in vacuo. The dark brown, amorphous mass gives off water and hydrogen chloride at 100°. I. L. Kondakoff and co-workers, and L. F. Nilson said that the aq. soln. contains hydrochloroplatinous acid. C. Liebermann and C. Paal obtained salts with organic bases ; and some ammines have been prepared—*vide infra.* Platinous hydrotrichloride loses a mol. of hydrogen chloride in vacuo at 100°, and with a protracted exposure some water is also given off. P. Klason said that platinous hydrotrichloride is not a chemical individual, but rather a mixture of platinum dichloride and tetrahydrated hydrochloroplatinous acid.

J. J. Berzelius, L. N. Vauquelin and G. Magnus dissolved platinous chloride in boiling hydrochloric acid with exclusion of air. The soln. dried in vacuo furnishes **platinous dihydrotetrachloride,** $PtCl_2.2HCl.nH_2O$, or, according to P. Klason, **hydrochloroplatinous acid,** $H_2PtCl_4.4H_2O$. J. Thomsen showed that a soln. of this salt can be obtained by treating a hot, sat. soln. of potassium chloroplatinite with the theoretical quantity of hydrochloroplatinic acid, and filtering from the precipitated potassium chloroplatinate. The heat of formation is ($Pt,Cl_2,2HCl,Aq.$)$=41\cdot83$ Cals. ; and ($Pt,O,4HCl,Aq.$)$=31\cdot55$ Cals. L. Pigeon did not obtain satisfactory results by reducing hydrochloroplatinic acid with sulphurous acid since it is difficult to determine whether the reduction has gone too far, or not far enough ; but he obtained a soln. by treating a soln. of a mol. of hydrochloroplatinic acid with a mol. of dry barium carbonate, and a mol. of barium dithionate with 3 times its weight of hot water, heating the mixture on a water-bath at 100°, and filtering the liquor. L. F. Nilson heated hydrochloroplatinic acid on a sand-bath at 300° until the dish and contents had the weight required for platinous chloride. The unconverted platinum tetrachloride was extracted with hot water, and the residue dissolved in hot, conc. hydrochloric acid. L. Pigeon said that the soln. cannot be crystallized, and he preferred to convert it into potassium chloroplatinite by the addition of potassium chloride.

L. N. Vauquelin observed that on evaporating the soln., brown platinous chloride is formed. L. F. Nilson, and A. Miolati and U. Pendini recommended evaporating the soln. first at 50°, and then in vacuo, and drying the product over sulphuric acid and potassium hydroxide in vacuo. L. Wöhler and F. Martin found that the salt is stable in hydrochloric acid soln. ; no separation of platinum was observed after it had been heated 10 hrs. in a sealed tube. If hydrochloric acid be not in excess, the soln. readily forms platinum and hydrochloroplatinic acid. It is supposed that the hydrochloroplatinous acid forms **hydrodichloroxyplatinic acid,** H_2PtOCl_2, which then decomposes into platinum and platinic chloride, $PtCl_4.H_2O$. Whilst solid platinous chloride can be heated to 600° or 700° in chlorine for many hours at atm. press., the salt decomposes when the aq. soln. is heated in a sealed tube at 120°. T. Curtius and J. Rissom observed that a soln. of potassium azide furnishes brownish-red **potassium azidoplatinite.** L. N. Vauquelin observed that sodium hydroxide precipitates from the soln. hydrated platinous

oxide. The **chloroplatinites** were studied by L. F. Nilson, who arranged them in 4 groups typified by: $2RCl.PtCl_2$, $R''Cl_2.PtCl_2$, $2R'''Cl_3.3PtCl_2$, and $R''''Cl_4.2PtCl_2$. The chloroplatinites were prepared either by decomposing barium chloroplatinite with the sulphate of the metal whose chloroplatinite is to be prepared, or else by treatment of an hydroxide with hydrochloroplatinous acid. The chloroplatinites are usually very soluble in water; they are for the most part deliquescent, and crystallize only from very conc. soln.; but few of them are without water of crystallization. At 100°, they are decomposed, with production of metallic platinum, a few evolving hydrochloric acid. By evaporating their soln. in presence of hydrochloric acid, the platinum is usually partially converted into platinic chloride—*vide infra.*

W. Peters [4] found that a mol. of platinous chloride at 20° to 26°, and 749 to 754 mm. press. slowly absorbs about 5 mols. of ammonia, and at the same time changes to a white or pale grey **platinous pentamminochloride,** $Pt(NH_3)_5Cl_2$; and if this product be kept in vacuo, **platinous tetramminodichloride,** $[Pt(NH_3)_4]Cl_2.H_2O$, is formed. J. Reiset prepared platinous tetramminochloride by boiling platinous chloride with aq. ammonia, with frequent additions of more ammonia, until the first-formed green $[Pt(NH_3)_4]PtCl_4$ redissolves, and then evaporating the soln. for crystallization. A similar process was employed by M. Peyrone, P. T. Cleve, and C. Grimm. M. Peyrone saturated the soln. of platinous chloride with aq. ammonia, in the cold, dissolved the precipitate in boiling hydrochloric acid, treated the filtrate with alcohol, washed with alcohol, and purified by recrystallization from cold water. P. T. Cleve, P. Klason, C. W. Blomstrand, and H. and A. Euler described **platinous dichlorotetrammine,** $Pt(NH_3)_4Cl_2$, formed by the action of hydrochloric acid on the corresponding hydroxide, and by the action of the calculated quantity of hydrochloroplatinous acid on ammonium diamminotetrachloroplatinite. The black powder dissolves in hydrochloric acid, forming platinous *cis*-dichlorodiammine. S. M. Jörgensen recommended:

The filtered soln. of 20 grms. of ammonium chloroplatinite in 100 c.c. of cold water and 50 c.c. of N-NH_4OH, is allowed to stand in a covered flask, in ice-water for 18 hrs. Add 100 c.c. 20 per cent. aq. ammonia, warm the mixture for some minutes on the water-bath until all the $[Pt(NH_3)_4]PtCl_4$ has dissolved, filter and cool. Triturate the product three times with 100 c.c. of cold 80 per cent. alcohol to remove the ammonium chloride, dissolve the residue in 45 c.c. of warm water, and when the filtered liquid is cool, add 4 vols. of absolute alcohol, and allow the flask to stand for half an hour in cold water. Wash the white product on a suction filter three times with 80 per cent. alcohol, and once with absolute alcohol, and dry it in air—Yield 15·0 grms.

J. Thomsen obtained platinous tetramminochloride by reducing finely-divided platinic dichlorotetramminochloride with hydrogen sulphide; L. Ramberg, by dissolving in boiling aq. ammonia the precipitate obtained by the action of ammonia on platinum chloroplatinite, and evaporating the filtered soln; J. Reiset, from a soln. of platinous *cis*- or *trans*-dichlorodiammine in aq. ammonia; C. Claus, and S. M. Jörgensen, from the mother-liquor obtained in preparing $[Pt(NH_3)_4]PtCl_4$; and O. Carlgren, and O. Carlgren and P. T. Cleve, by slowly evaporating a soln. of $[(NH_3)_3Pt(NH)_2Pt(NH_3)_3]SO_4[Pt(NH_3)_4]SO_4$ in hydrochloric acid.

E. Koefoed obtained what he considered to be an isomeric form of platinous tetramminochloride from platinous *cis*-dichlorodiammine and ammonia; or by boiling platinous tetramminochloroplatinite with ammonia. The amber-yellow crystals have a greenish sheen. When the salt is treated with hydrochloric acid, some platinous chlorotriamminochloride is formed. Alcohol precipitates the salt unchanged from its aq. soln. Platinous chloride converts it into the tetramminochloroplatinite.

H. Kolbe, C. W. Blomstrand, W. Odling, C. Gerhardt, A. Hantzsch and F. Rosenblatt, C. Weltzien, A. W. Hofmann, C. Claus, A. Werner, and P. Klason studied the constitution of the compound; and A. Rosenheim and L. Gerb, and H. D. K. Drew and co-workers studied the stereochemistry of the tetrammines.

M. Peyrone, A. M. Boldyreva, and P. T. Cleve observed that the salt furnishes colourless, tetragonal crystals with a salty taste, and that the crystals have no action on litmus paper. Q. Sella found that the tetragonal crystals have the axial ratio $a : c = 1 : 0{\cdot}5623$, no marked cleavage, and negative double refraction. N. S. Kurnakoff and I. A. Andrejewsky gave $a : c = 1 : 0{\cdot}566$, and said that there is no appreciable cleavage; that the double refraction is weak and negative; and that the indices of refraction are $\omega = 1{\cdot}672$, and $\epsilon = 1{\cdot}667$. H. D. K. Drew and co-workers found that the X-radiograms of the salts prepared from the α- or β-diammine are the same. The tetragonal lattice of the monohydrate has $a = 7{\cdot}30$ A., and $c = 4{\cdot}23$ A.; and probably D_4^1 or D_{4b}^1. The evidence obtained so far seems to indicate that the four ammonia groups are situated at the corners of a square around the platinum atom, the water molecules lying midway between platinum atoms in a direction inclined to the plane of the ammonias. Observations were also made by A. M. Boldyreva, E. G. Cox and G. H. Preston, and B. N. Dickinson —*vide* the palladium analogue. E. G. Cox gave $a = 7{\cdot}39$ A., $c = 4{\cdot}21$ A., and $a : c = 1 : 0{\cdot}570$. The distances $Pt : Pt = 4{\cdot}21$ A., $Pt : NH_3 = 2{\cdot}62$ A., $Cl : NH_3 = 3{\cdot}36$ A., and $Pt : Cl = 4{\cdot}25$ A. The 4 covalencies in the complex $[Pt(NH_3)_4]$ are co-planar, and directed to the 4 corners of a square. R. Lorenz and I. Posen gave 2·737 for the sp. gr. of $[Pt(NH_3)_4]Cl_2$. N. S. Kurnakoff gave for the sp. gr. of a 7·166 per cent. soln., 1·05095 at 19·1°/4°. P. T. Cleve said that the crystals lose all their water at 100°, and J. Reiset, that 4·88 per cent. is lost at 110°, and on exposing the product to air, the water is rapidly taken up again. Large crystals which have been dehydrated may decrepitate on cooling. When heated to about 250°, ammonia is evolved, and there remains platinous diamminochloride; at a higher temp., ammonium chloride, and hydrogen chloride are given off, and platinum remains. A. A. Grinberg and B. V. Pittsin studied the subject. M. Peyrone said that the evolution of ammonia begins at 220°, and becomes energetic at 240°, and a soln. of the product in hot water yields crystals of dichlorodiammine. E. N. Gapon measured the diffusion coeff. J. Petersen gave 0·275° for the lowering of the f.p. of a 1·837 per cent. soln. J. Thomsen found the heat of soln. to be −8756 cals. N. Kurnakoff gave for the coeff. of refraction of a 7·166 per cent. soln., 1·33993 for Li-light; 1·34217 for Na-light; and 1·34519 for Tl-light; the mol. refraction with the μ-formula is 74·1; and the at. refraction of platinum is between 11·9 and 16·7. A. Werner and A. Miolati found the mol. conductivity of a mol of the salt in 500, 1000, and 2000 litres of water to be, respectively, 247·6, 260·8, and 267·2. R. Lorenz and I. Posen found the eq. conductivity, λ, of a mol of the salt in v litres to be:

v . . .	32	64	128	256	512	1024	∞
λ . . .	121·2	128·8	133·7	137·9	140·9	144·7	150·8

The ionic velocity of the complex $[Pt(NH_3)_4]^{\cdot\cdot}$ is 37·8; for the complex $[Pten_2]^{\cdot\cdot}$, 32·0; for *cis*-$[Pt(NH_3)_2py_2]^{\cdot\cdot}$, 25·8; and for $[Ptpy_4]^{\cdot\cdot}$, 21·0.

J. Reiset, and P. T. Cleve found that a sat. soln. contains 20 per cent. of the salt at 16·5°, and that the solubility increases with a rise of temp. N. S. Kurnakoff and I. A. Andrejewsky observed that when recrystallized from water a few times, the product is a solid soln. of isomorphous $PtCl_2(NH_3)_4.H_2O$ and $PtCl_2(NH_3)_2.4PtCl_2(NH_3)_4$. J. Reiset observed that if *chlorine* is passed into the aq. soln., platinic dichlorotetramminochloride is formed; and P. T. Cleve, that *iodine* forms no definite compound, but only a mixture; and M. Peyrone, that when evaporated with *hydrochloric acid*, in excess, ammonium chloride and platinous *trans*-dichlorodiammine are formed. L. Tschugaeff and S. Krassikoff studied the action of *sulphur dioxide*. A. R. Klien studied the action of water, acids, and alkaline soln. M. Peyrone also noted that *sulphuric acid* or *nitric acid* introduces the sulphate or nitrate radicle in place of the chloride radicle; and J. Reiset added that with hot nitric acid, platinic dichlorotetramminonitrate is formed. I. I. Shukoff and O. P. Schipulina studied the adsorption of the salt by *charcoal*,

and the adsorption of the tetrammine on charcoal, and likewise compared the results with other members of that series of complex salts. The addition of *alcohol* or *ether* to the aq. soln. precipitates the original salt as a white, crystalline powder. M. Peyrone observed that *oxalic acid* converts the chloride into an oxalate. H. Kautsky and W. Baumeister studied the adsorption of the $[Pt(NH_3)_4]^{\cdot\cdot}$-ions by *silicic acid*. J. Reiset found that a little ammonia is expelled when a soln. of the salt is heated with *alkali lye* ; and M. Peyrone, that *potassium carbonate* decomposes the salt slowly in the cold, rapidly at 40° to 50°, forming potassium chloride, and the tetramminocarbonate. J. Reiset found that with soluble *silver salts*, silver chloride is precipitated and the corresponding salt of the tetrammine is formed. M. Peyrone said that the reaction with *potassium amalgam* can be symbolized : $K_2Hg_n+[Pt(NH_3)_4]Cl_2=2KCl+4NH_3.PtHg_n$ (black powder). S. Aoyama found that copper precipitates all the platinum from an acidic soln. N. S. Kurnakoff and I. A. Andrejewsky observed that **platinous dichlorodiamminedichlorotetramminoplatinite,** $PtCl_2(NH_3)_2.4PtCl_2(NH_3)_4$, is isomorphous with $PtCl_2(NH_3)_4.nH_2O$. A. M. Boldyreva studied the tetragonal crystals. G. B. Buckton found that a soln. of *stannous chloride* produces a voluminous, white precipitate which dissolves on warming ; and when this soln. is cooled, the precipitate which is formed contains stannic oxide ; if the soln. is heated a red soln. is formed, along with ammonium chloride and a precipitate of platinum and stannic oxide. With *ferric chloride*, platinic dichlorodiamminochloride and ferrous chloride are formed. According to M. Peyrone, *platinous chloride* in aq. soln. forms platinous tetramminochloroplatinite, $[Pt(NH_3)_4]Cl_2.PtCl_2$; J. Reiset, that an excess of *hydrochloroplatinic acid* gives an olive-green precipitate of platinous tetramminochloroplatinate, $[Pt(NH_3)_4]Cl_2.PtCl_4$, which, according to P. T. Cleve, is mixed with some platinous tetramminotetrachloride and platinic dichlorotetramminochloride. These reactions were studied by A. Cossa. E. G. Cox could not confirm the conclusion of N. S. Kurnakoff and I. A. Andrejewsky that the tetrammine forms a solid soln. with the diammine—$4\{Pt(NH_3)_4Cl_2\}Pt(NH_3)_2Cl_2$.

Platinous tetramminochloride forms a series of double salts with other metal chlorides. Thus, G. B. Buckton, and C. W. Blomstrand described **platinous tetramminochlorocuprate,** $[Pt(NH_3)_4]CuCl_4$; G. B. Buckton, **platinous tetramminochlorobarytate,** $[Pt(NH_3)_4]BaCl_4$; **platinous tetramminochlorozincate,** $[Pt(NH_3)_4]ZnCl_4$; **platinous tetramminochloromercurate,** $[Pt(NH_3)_4]HgCl_4$; **platinous tetramminochlorostannite,** $[Pt(NH_3)_4]SnCl_4$; **platinous tetramminochlorostannate,** $[Pt(NH_3)_4]SnCl_6$; **platinous tetramminochloroplumbate,** $[Pt(NH_3)_4]PbCl_4$; and N. S. Kurnakoff, **platinous tetramminochlorocobaltate,** $[Pt(NH_3)_4]CoCl_4$.

The corresponding **platinous tetramminochloroplatinite,** $[Pt(NH_3)_4]PtCl_4$, also called *Magnus' green salt*, was prepared by G. Magnus by saturating a soln. of brown platinous chloride in hydrochloric acid with aq. ammonia, and allowing it to stand for some time. J. Gros, and C. Claus also saturated a soln. of hydrochloroplatinous acid with aq. ammonia. L. Ramberg used a similar process. A. Cossa obtained the salt from a mixture of platinous chloride with platinic chloride and platinic tetramminochloride, and also by the action of platinous tetramminochloroplatinate on potassium chloroplatinite ; P. T. Cleve, by mixing conc. soln. of platinous chloride and hydrochloroplatinic acid, and from a mixture of potassium chloroplatinite and platinic chlorohydroxytetramminonitrate ; M. Peyrone, by adding platinous chloride to the mother-liquor left after preparing platinous tetramminochloride ; F. W. Clarke and M. E. Owens, and L. Ramberg, by adding a soln. of potassium chloroplatinite to aq. ammonia ; and L. Tschugaeff and W. Subbotin, by shaking for 3 or 4 hrs. a mixture of platinous chloride with platinous tetralkylsulphinochloroplatinite. S. P. Sharples obtained it by boiling a soln. of platinous chloride with platinum black, and then adding aq. ammonia, and alcohol to the liquid. H. and W. Biltz recommended the following process :

Reduce a hot soln. of 2 grms. of hydrochloroplatinic acid in 7 c.c. of water by adding sulphurous acid a little at a time, and towards the end, drop by drop; wait before each addition until the odour of sulphurous acid has entirely disappeared—towards the end of the operation this requires some time—and test if a drop of the reddish-yellow soln. gives a precipitate when brought in contact with a conc. soln. of ammonium chloride on a watch-glass. An excess of sulphurous acid would decolorize the soln. and form hydrosulphitoplatinous acid. When no precipitate or only a slight one is produced by the ammonium chloride, boil the soln. of hydrochloroplatinous acid so prepared, and add an excess of conc. aq. ammonia. Magnus' green salt is precipitated in acicular crystals. The precipitation continues as the soln. cools, and sometines there is also formed a little yellow, crystalline platinous dichlorodiammine which does not settle so readily and can be decanted off with the water. Drain off the salt by suction, and wash successively with water, alcohol, and ether. The yield 0·25 grm. is small because most of the platinum remains in the mother-liquor as platinous tetramminochloride. Add to this soln. three times its vol. of alcohol, redissolve the precipitate in 30 c.c. of hot water, precipitate the platinum tetramminochloroplatinite from this boiling soln. by adding hydrochloroplatinous acid until no more green precipitate is formed. The total yield is about 1·3 grms. when the theoretical yield is 1·7 grms.

The crystals of platinous tetramminochloroplatinite were described by M. Raewsky, M. Peyrone, and P. T. Cleve as dark green needles or prisms. A. M. Boldyreva said that the crystals are tetragonal and uniaxial. E. Hertel and K. Schneider found that the space-lattice of the green, tetragonal crystals has a=6·297 A., c=5·15 A., and $a:c$=1 : 0·8175, but E. G. Cox and co-workers found that the structure has the $PtCl_4$- and $Pt(NH_3)_4$-groups of the same form as those in potassium chloroplatinite, and in $[Pt(NH_3)_4]Cl_2$, excepting that the NH_3-groups in the cation are not rotary. The tetragonal crystals have the cell dimensions a=6·29 A., and c=6·42 A., each NH_3-group is at a distance 3·74 A. from four chlorine atoms, and 3·68 A. from two. The sp. gr. is less than 4·1; the calculated value is 3·9 with 1 mol. of $[Pt(NH_3)_4]PtCl_4$ in the unit cell. E. Hertel studied the subject. J. Gros said that when heated the salt gives off some vapours of ammonium chloride, etc.; and platinum remains behind. L. Tschugaeff and N. Pschenicyn studied the depolymerization symbolized: $[Pt(NH_3)_4]PtCl_4 = 2[Pt(NH_3)_2Cl_2]$. N. R. Dhar found the mol. conductivity of an aq. soln. of a mol of the salt in 4050, 6750, 20,250, and 60,750 litres of water to be, respectively, 566·67, 640·56, 647·32, and 650·90. P. T. Cleve said that the salt is very sparingly soluble in water. L. Tschugaeff and I. Tscherniaeff oxidized Magnus' salt with ammonium persulphate, and obtained $(Pt,4NH_3)_2(SO_4)(PtCl_4)_2(OH)_2$; and with nitric acid in the presence of hydrogen dioxide, $[Pt,4NH_3,(NO_3)]PtCl_4$. C. Gerhardt observed that chlorine converts it into $[Pt(NH_3)_4Cl_2]PtCl_4$ and then into $[Pt(NH_3)_4Cl_2]PtCl_6$. G. Magnus added that the aq. soln. is not decomposed by hydrochloric acid, and J. Gros, that boiling hydrochloric acid or sulphuric acid takes up no ammonia. J. Gros, and M. Raewsky found that nitric acid converts the salt into $[Pt(NH_3)_4Cl_2](NO_3)_2$ and $[Pt(NH_3)_4(OH)Cl](NO_3)_2$; and A. Cossa, that ammonium nitrate forms a mixture of different compounds, $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$, $[Pt(NH_3)_4Cl_2](NO_3)_2$, and $[Pt(NH_3)_2Cl_2]$. J. Reiset found that boiling ammonia converts the salt into platinous tetramminochloride. I. I. Shukoff and O. P. Schipulina observed that the salt is decomposed when it is adsorbed by carbon. F. W. Clarke and M. E. Owens showed that the salt forms a brown soln. with hot aq. potassium cyanate. J. Gros observed no evolution of ammonia occurs when the salt is boiled with an aq. soln. of potassium hydroxide. P. T. Cleve showed that silver nitrate forms silver chloroplatinite and platinous tetramminonitrate; and J. Reiset, that boiling hydrochloroplatinic acid forms platinous chloride, and $[Pt(NH_3)_4Cl_2]PtCl_4$. The constitution of the green platinous tetramminochloroplatinite was discussed by C. Weltzien, and M. Peyrone.

S. M. Jörgensen and S. P. L. Sörensen observed that in preparing the green salt by the action of potassium chloroplatinite on platinous dichlorodiammine, a *red isomeride* may be formed. The conditions favourable for the production of the red salt are: the absence of potassium chloroplatinate often present in traces in the platinous salt, and a very dil. neutral or slightly ammoniacal soln. in the

presence of a large excess of water. The formation of the green salt is favoured by the use of concentrated solutions or of solutions acidified with hydrochloric acid. E. G. Cox and co-workers prepared the pink salt by treating an aq. soln. of $[Pt(NH_3)_4]Cl_2$ with a quarter of its vol. of aq. ammonia of sp. gr. 0·88, and then with a neutral soln. of potassium chloroplatinite free from chloroplatinate. A good yield of the pink salt is deposited, and it is contaminated with a little green salt. According to S. M. Jörgensen and S. P. L. Sörensen, the precipitate should be washed with aq. alcohol, and finally with absolute alcohol; it furnishes small, ill-defined needles, rose-red in colour. The same salt is obtained in well-defined, small, tetragonal prisms by interaction of the yellow platinous dimethylamine-amminochloroplatinite with platinous dichlorodiammine. E. Hertel and K. Schneider found that the space-lattice of the red, tetragonal crystals has a=6·293 A., c=5·25 A., and $a : c$=1 : 0·8340. E. G. Cox and co-workers said that these results are wrong. The crystals are rhombic and have a space-lattice with a=7·9 A., b=8·2 A., and c=7·9 A.; the calculated sp. gr. is 3·9, when there are two mols. of $[Pt(NH_3)_4]PtCl_4$ per unit cell. The red and green salts are anhydrous, and in the dry condition they are very stable, but on boiling the red salt with water it is changed quantitatively into the green salt; the converse change has not been observed. E. G. Cox and co-workers found that when examined by X-radiograms or by the microscope the pink salt of Magnus is indistinguishable from the empirically isomeric Cleve's salt, $[Pt(NH_3)_3Cl]_2PtCl_4$. According to H. D. K. Drew and H. J. Tress, the triammine is (i) more soluble in water than the pink salt of Magnus; (ii) a cold aq. soln. of sodium nitrate rapidly changes the red to the green salt, but it does not affect the colour of the triammine; (iii) a lukewarm aq. soln. of $[Pt(NH_3)_4]Cl_2$ liberates the triammine from its platinous salt with the precipitation of the green salt of Magnus, whereas with the red tetrammine, there is no action for some time, and if, on heating, the red salt becomes green, only the tetrammine, and no triammine is found in the filtrate; and (iv) when the two salts are treated with a cold aq. soln. of silver nitrate, silver chloroplatinite is precipitated. On removing the excess of silver with a soluble chloride, and treating the liquids with an aqueous soln. of potassium chloroplatinite, in the one case, the initial triammine is regenerated in red plates, and in the other case, acicular crystals of the green salt are formed. With potassium chloropalladite so used instead of the chloroplatinite, the triammine furnishes **platinous chlorotriamminochloropalladite,** $[Pt(NH_3)_3Cl]_2PdCl_4$, whereas the red salt of Magnus gave greyish-pink needles of **platinous tetramminochloropalladite,** $[Pt(NH_4)_4]PdCl_4$. The evidence shows that there is no connection between the red platinous triammine and the red form of Magnus' salt.

The red and green salts of Magnus appear to be similar in crystalline form when viewed under the microscope; their solubilities are similar; no difference has been detected in the chemical reactions; they have the same molecular weights; dichroism does not explain their occurrence; and nothing has yet been observed to show any difference in chemical structure. No other pair of red and green isomeric platinous salts is known, but the substitution of the four ammonia residues in $[Pt(NH_3)_4]PtCl_4$ by methyl-, *n*-butyl-, *iso*-butyl-, or amyl- amine forms a green salt, whereas a similar substitution of ethyl- or of *n*-propyl-amine gives a red salt, but **platinous tetraethylaminochloroplatinite,** $[Pt(C_2H_5NH_2)_4]PtCl_4$, is green.

H. D. K. Drew and co-workers prepared **platinous tetramminochloropalladite,** $[Pt(NH_3)_4]PdCl_4$, in lilac-grey needles. J. Reiset prepared **platinous tetrammino-chloroplatinate,** $[Pt(NH_3)_4]PtCl_6$, as a red, crystalline mass by the action of an excess of platinic chloride on platinous tetramminochloride, but P. T. Cleve said that $[Pt(NH_3)_4Cl_2]PtCl_4$ is produced by this process. A. Cossa, however, obtained it by adding, at ordinary temp., a neutral soln. of platinic chloride, or of sodium chloroplatinate, to a soln. of platinous tetramminochloride. The yellow, amorphous product slowly passes into $[Pt(NH_3)_4Cl_2]PtCl_4$, and the change is rapid with boiling

soln. P. Schützenberger and D. Tommasi described **platinous biscarbonyldiamminochloride,** $[Pt(NH_3)_2(CO)_2]Cl_2$.

E. A. Hadow, and S. M. Jörgensen obtained a double salt, **platinous tetramminodinitratotetramminochloroplatinate,** $2[Pt(NH_3)_4]PtCl_4.[Pt(NH_3)_4(NO_2)_2]PtCl_4$; and the triple salt, **platinous tetramminosulphitochloroplatinite,** $2[Pt(NH_3)_4]Cl_2.PtSO_3.PtCl_2$. A. Cossa, and S. M. Jörgensen obtained **platinous tetramminotrichloroamminoplatinite,** $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$; S. M. Jörgensen, **platinous tetramminotrichloroethylamineplatinite,** $[Pt(NH_3)_4][Pt(C_2H_5NH_2)Cl_3]_2$; **platinous tetramminotrichloropyridineplatinite,** $[Pt(NH_3)_4][Pt(C_5H_5N)Cl_3]_2$; **platinous tetramminotrichloroethyleneplatinite,** $[Pt(NH_3)_4][Pt(C_2H_4)Cl_3]_2$; and **platinous tetramminotrichloroallylalcoholoplatinite,** $[Pt(NH_3)_4][Pt(C_3H_5OH)Cl_3]_2$.

L. Tschugaeff and I. Tscherniaeff prepared derivatives of **platinous aquotriamminochloride,** $[Pt(NH_3)_3(H_2O)]Cl_2$, by passing air through a soln. of the dihydroxylaminoamminochloride containing ammonia and ammonium sulphate, or any other sulphate, and a trace of a copper salt. The colourless precipitate—possibly $(NH_3)_4Pt....(OH)_2....Pt(NH_3)_4$—is soluble in warm dil. sulphuric acid, and when the soln. is treated with platinous chloride, **platinous aquotriamminochloroplatinite,** $[Pt(NH_3)_3(H_2O)]PtCl_4$, is formed in green needles. When this salt is warmed with hydrochloric acid, or a soluble chloride, it forms the chlorotriammine, $[Pt(NH_3)_3Cl]_2PtCl_4$.

A. Cossa [5] prepared **platinous chlorotriamminochloride,** $[Pt(NH_3)_3Cl]Cl$, from a mixed soln. of the corresponding nitrate and conc. hydrochloric acid by cooling it with ice, drying the crystals between bibulous paper, recrystallizing from aq. soln., and drying at 100°. P. Klason heated a mixture of equimolar proportions of platinous tetramminochloride and hydrochloric acid at 108°, allowing the platinous *trans*-dichlorodiammine to crystallize out, then added potassium chloroplatinite to precipitate the unchanged tetramminochloride from the boiling soln., and there remained the chlorotriamminochloride. P. Klason obtained a bad yield by treating the *cis*-dichlorodiammine with ammonia. A. Cossa prepared the salt by adding ammonia to green platinous tetramminochloroplatinite, platinous *cis*- or *trans*-dichlorodiammine, or to platinum trichlorotriammine; and he recommended mixing a boiling soln. of platinous chlorotriamminochloroplatinite with a soln. of platinous tetramminochloride, filtering, and evaporating for crystallization. The salt appears in colourless scales or prisms which, according to A. Cossa, belong to the monoclinic system. A. Werner and A. Miolati found that the mol. conductivities of a soln. of a mol of the salt in 250, 500, 1000, and 2000 litres of water, are, respectively, 101·0, 107·6, 115·8, and 127·8. The constitution of the salt was discussed by P. T. Cleve, and P. Klason. P. Klason found that the salt is hydrolyzed in aq. soln. P. T. Cleve observed that chlorine converts it into $[Pt(NH_3)_3Cl_3]Cl$; A. Cossa, that hydrochloric acid forms platinous *cis*-dichlorodiammine, and ammonia furnishes platinous tetramminochloride. The salt is insoluble in alcohol. P. Klason noted the formation of the complexes platinous chloroethylsulphodiamminochloride, $[Pt(NH_3)_2(SC_2H_5)Cl]$; and platinous bisphenylsulphodiammine, $[Pt(NH_3)_2(SC_6H_5)_2]$. P. T. Cleve noted that potassium chloroplatinite forms platinous chlorotriamminochloroplatinite, and A. Cossa, that sodium chloroplatinate forms platinous chlorotriamminochloroplatinate.

M. Peyrone obtained a small yield of **platinous chlorotriamminochloroplatinite,** or *Cleve's salt*, $[Pt(NH_3)_3Cl]PtCl_4$, by adding ammonium carbonate to a very dilute, neutral, boiling soln. of platinous chloride. P. T. Cleve treated a hydrochloric acid soln. of platinous chloride with ammonia and found that insoluble platinous chlorotriamminochloroplatinite, and tetramminochloroplatinite and soluble platinous tetramminochloride and chlorotriamminochloride were formed, and he also obtained it from soln. of platinous triammino-salts and platinous chloride. L. Ramberg obtained it by the action of ammonia on potassium chloroplatinite in the presence of ammonium chloride. A. Cossa heated a soln. of 10 grms. of platinous tetramminochloride in 50 c.c. of water with 75 c.c. of hydrochloric acid of sp. gr. 1·198 at 20°, in a reflux condenser in boiling water, filtered

the cold soln. from the platinous diamminodichloride; added potassium chloroplatinite and filtered from the platinous tetramminochloroplatinite and evaporated the soln., and obtained a yield of 2·70 grms. of platinous chlorotriamminochloroplatinite in rose-red, lustrous plates or scales. The general methods depend on adding ammonia to the dichlorodiammine, or removing ammonia from the tetramminochloride. L. Tschugaeff prevented the ammonation of the dichlorodiammine being carried too far, by employing potassium cyanate which evolves ammonia gradually when hydrolyzed:

One grm. of platinous *cis*-dichlorodiammine (Peyrone's chloride) is boiled with 0·7 grm. of potassium cyanate and 18 to 20 c.c. of water. After soln. is complete the boiling is continued for one minute. Several portions prepared in this way are combined, and heated with an excess of hydrochloric acid, sp. gr. 1·19 (4 c.c. for each portion); the whole is then heated to boiling, and cooled. After collecting the unchanged dichlorodiammine which separates, an excess of potassium chloroplatinite is added to the filtrate, whereby a mixture of platinous tetramminochloroplatinite and of platinous chlorotriamminochloroplatinite is formed. This mixture is then separated by taking advantage of the fact that the latter compound is fairly readily soluble in hot water. The yield of chloroplatinite thus obtained is about 50 per cent. of the theoretical, calculated on the dichlorodiammine which enters into reaction.

E. G. Cox and co-workers found that the pink salt of Magnus is formed only under special conditions, and that the salt usually called the pink salt of Magnus is really Cleve's salt. The X-radiograms of the two salts are very similar. The c-axes of the two are equal, and the a-axis of Cleve's salt is probably 3 or $3/\sqrt{2}$ times that of the tetrammine salt.

A. R. Klien studied the action of water, acids, and alkalies on the salt. Platinous chlorotriamminochloroplatinite is soluble in cold water, and freely soluble in boiling water; it is not decomposed by boiling water; ammonia transforms it into platinous tetramminochloroplatinite; nitric acid yields platinic chlorodinitratotriamminochloride; silver nitrate precipitates silver chloroplatinite, and forms a soln. of platinous nitratotriamminonitrate; silver sulphate forms platinous sulphatotriammine; potassium permanganate in a boiling soln. forms **platinous chlorotriamminochloroplatinate,** $[Pt(NH_3)_4Cl][PtCl_6$, with sodium chloroplatinate. A. Cossa observed that there is formed platinous chlorotriamminochloroplatinate. M. Peyrone prepared **platinous chlorotriamminotrichloroamminoplatinite,** $[Pt(NH_3)_3Cl][Pt(NH_3)Cl_3]$.

W. Odling[6] prepared yellow **platinous *trans*-dichlorodiammine,** $[Pt(NH_3)_2Cl_2]$, by the action of hydrochloric acid on the corresponding hydroxide, Reiset's second base; and also by the action of ammonia on platinous chloride. This salt has also been called *Reiset's chloride,* and **platinous α-dichlorodiammine.** J. Reiset, M. Peyrone, P. T. Cleve, and L. Ramberg prepared it by heating platinous tetramminochloride to 250° as long as ammonia is evolved, and until a white cloud of ammonium chloride appears. The residue can be crystallized twice from hot water, or transformed into the nitrate, by treatment with silver nitrate, and the filtrate treated with hydrochloric acid. Just as J. Reiset obtained the salt by heating platinous dinitrato- or sulphato-diammine with hydrochloric acid or alkali chloride, M. Peyrone evaporated to dryness a mixture of platinous tetramminochloride and an excess of conc. hydrochloric acid, and extracted the ammonium chloride with water; and J. Reiset, also, by boiling platinous tetramminochloroplatinite for a long time with a soln. of ammonium nitrate, sulphate, or chloride, and cooling the liquid. A. Cossa observed that some $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$, previously described, is formed. S. M. Jörgensen found that dichlorodiammine is formed in the thermal decomposition of ammonium chloroplatinite at 170°. H. and W. Biltz recommended the following process:

Heat about 0·3 grm. of platinous tetramminochloride to 250° in a test-tube immersed in a paraffin bath. If any water is given off, stop the heating to remove the drops, condensed on the upper walls of the test-tube, by a strip of filter-paper. Continue the heating until ammonia is evolved, the substance becomes dark coloured, and a brittle platinum

black begins to deposit on the glass. The treatment occupies about 20 mins. Extract the greyish-yellow mass in a beaker with 20 c.c. of boiling water; and filter the hot pale yellow soln., from the black residue. On cooling, a mass of pale yellow crystals of the trans-salt is deposited from the soln. Drain the crystals, wash with alcohol, then with ether, and allow them to dry. Yield 0·1 grm.

The colour of the trans-salt ranges from a pale yellow to a sulphur yellow. It may occur in acicular crystals, or, according to A. Cossa, in rhombic, hexagonal plates. A. M. Boldyreva said that the crystals are tetragonal and uniaxial. H. D. K. Drew and co-workers found that the pale yellow crystals are tabular, and often elongated, and twinning is common. The crystals have a straight extinction; positive elongation; and refractive index 1·76. M. Peyrone said that the salt decomposed at about 270° into ammonium chloride, hydrogen chloride, nitrogen and platinum. J. Lifschitz and E. Rosenbohm studied the optical properties. A. Werner and A. Miolati found the mol. conductivities of soln. with a mol of the salt in 500 and 1000 litres of water are respectively 22·60 and 22·42. A. Werner and C. Herty said that the electrical conductivity of the soln. is characteristic of that of a non-ionized salt. H. D. K. Drew and co-workers found that the conductivity increases rapidly with time, so that the mol. conductivities, μ, of soln. with a mol. of the β-salt in 2866 and 1234 litres, respectively, were:

Time	0	62	131	174	2752
μ $v=2866$	7·0	21·0	26·1	32·7	89·8
μ $v=1234$	7·5	9·0	11·2	14·1	38·7

They attributed the change to the destructive action of water generating ammonium chloride. A. Werner and A. Miolati made observations on the conductivity of soln. of the salt. The salt dissolves very slowly in water. W. Odling observed that the salt is very sparingly soluble in cold water; but is more soluble in hot water—M. Peyrone observed that 140 parts of boiling water dissolve 1 part of salt, and P. T. Cleve, that 130 parts of boiling water or 4472 parts of water at 0° are required to dissolve 1 part of salt. H. D. K. Drew and co-workers said that 100 grms. of water at 25° dissolve 0·036 grm. of the α-salt. The treatment of the salt with chlorine, aqua regia, or a mixture of potassium chlorate and hydrochloric acid furnishes citron-yellow, octahedra of platinic dichlorotetramminochloride; bromine furnishes a mixture containing platinous dibromodiammine, and similarly with iodine; with hot nitric acid, yellow fumes are evolved. L. Tschugaeff and W. Chlopin found that Reiset's chloride in the presence of ammonia and ammonium carbonate forms platinic chloropentamminochloride—*vide infra*, Peyrone's chloride; and that with hydrogen dioxide, hydroxy-compounds are formed. The salt is converted by aniline or ethylamine into platinous bisaniline diamminochloride or bisethylaminediamminochloride respectively. An excess of potassium cyanide dissolves the salt with the liberation of ammonia and the formation of potassium cyanidoplatinite. L. Ramberg studied the liberation of ammonia from the platinum ammines when they are treated with sodium hydroxide; and I. I. Shukoff and O. P. Shipulina, the adsorption of the salt by charcoal. A. Werner observed that when the salt is triturated with silver oxide, the resulting colourless alkaline fluid furnishes the *trans-salt* when treated with an excess of conc. hydrochloric acid. P. T. Cleve said that a soln. of silver nitrate does not precipitate all the chlorine. N. S. Kurnakoff found that thiocarbamide forms the complex salts $PtCl_2\{CS(NH_2)_2\}_4$, $PtCl_2\{CS(NH_2)_2\}_2$, and $PtCl_2.CS(NH_2)_2$; and that with pyridine there is formed $PtCl_2\{CS(NH_2)_2\}_2(C_5H_5N)_2$.

E. Koefoed reported that a *brown salt* of the same composition as that of the yellow salt just described is formed by boiling yellow platinous tetramminochloride with conc. hydrochloric acid; and by boiling a conc. soln. of platinous tetramminochloroplatinite in aq. ammonia, not too long with dil. hydrochloric acid, evaporating the soln. to dryness, treating the residue with hydrochloric acid (sp. gr. 1·19) and evaporating to dryness a few times, crystallizing from boiling water, and drying at 100°. The leather-brown crystals are sparingly soluble in water, but they are

more soluble than is the case with the yellow salt. The solubility of the salt in hot water is much greater, and with boiling water, the brown salt passes into the yellow form. Aqua regia, or a mixture of potassium permanganate and hydrochloric acid, form $[Pt(NH_3)_2Cl_4]$; potassium iodide furnishes $[Pt(NH_3)_2I_2]$; and ammonium sulphite gives crystalline needles of a double salt. F. Hoffmann prepared **platinous hydroxychlorodiammine,** $[Pt(NH_3)_2(OH)Cl]$; and A. R. Klien studied the salt. A. Grünberg and D. I. Rjabtschikoff prepared **platinous diaquodiamminochloride,** $[Pt(NH_3)_2(H_2O)_2]Cl_2$, and **platinous hydroxyaquodiamminochloride,** $[Pt(NH_3)_2(H_2O)(OH)]Cl$.

C. Grimm obtained a dark red, crystalline powder of what he regarded as *ammonium platinous dichlorodiamminochloride*, $2NH_4Cl.[Pt(NH_3)_2Cl_2]$, by crystallizing a soln. of platinous tetramminochloride with a large excess of ammonium chloride. N. S. Kurnakoff, and H. and A. Euler said that the product is probably impure platinic dichlorotetramminochloride (*q.v.*).

W. Odling obtained **platinous** ***cis*****-dichlorodiammine,** $[Pt(NH_3)_2Cl_2]$, or *Peyrone's chloride*, or **platinous β-dichlorodiammine,** by gently heating a soln. of platinous chloride, tetramminochloroplatinite, or *trans*-dichlorodiammine in aq. ammonia; and P. T. Cleve, by precipitation from a soln. of the corresponding nitrate or sulphate by the addition of hydrochloric acid or alkali chloride. P. T. Cleve also prepared it by adding ammonia to a brown soln. of platinous chloride in cold hydrochloric acid, boiling the greenish-yellow precipitate with water, when insoluble platinous tetramminochloroplatinite and a soln. of the *cis*-salt are formed. The soln. on cooling deposits the cis-salt. M. Peyrone prepared this salt by gently heating a soln. of platinous tetramminochloride in aq. ammonia, dissolving the precipitate in boiling hydrochloric acid, washing the precipitate with water to remove the tetramminochloride, and recrystallizing from a soln. in hot hydrochloric acid. M. Peyrone obtained the salt by pouring potash-lye into a soln. of platinous chloride neutralized with ammonium carbonate; he also prepared the salt from a soln. of platinous chloride in hydrochloric acid, and neutralized with ammonium carbonate, by boiling the soln. with an excess of ammonium carbonate, cooling the filtered liquid, and recrystallizing from hot aq. soln.

H. and W. Biltz recommended the following procedure for the cis-salt:

Prepare a soln. of hydrochloroplatinous acid from a gram of hydrochloroplatinic acid as indicated above in connection with platinous tetramminochloroplatinite. Concentrate the soln. to a vol. of about 2 c.c. and neutralize it while still warm with a conc. soln. of ammonium carbonate. Add an excess of the latter to make a total vol. of about 15 c.c. Boil the soln. The colour changes from a dark reddish-brown to an intense yellow, and at the same time green crystals of platinous tetramminochloroplatinite are deposited. Filter the boiling hot soln., and remove the yellow crystals which separate as the soln. cools. Rinse the crystals with alcohol, and ether, and recrystallize them from a few c.c. of boiling water. The product can then be obtained free from Magnus' green salt. The yield is less than 1 grm.

S. M. Jörgensen obtained the cis-salt by heating 1 part of ammonium chloroplatinite for many days with 25 parts of water in a sealed tube at 140°.

S. M. Jorgensen recommended mixing a filtered soln. of 20 grms. of ammonium chloroplatinite in 100 c.c. of cold water with 50 c.c. of $5N$-NH_4OH, and allowing the liquid to stand for 12 to 18 hrs. in ice-cold water. Wash the mixture of the cis-salt and platinous tetramminochloroplatinite with iced water until the filtrate gives no precipitate with potassium chloroplatinite. Wash the precipitate with boiling water. The tetramminochloroplatinite remains on the filter-paper. Mix the filtrate with one-third its vol. of dil. hydrochloric acid (1 : 1), and after the mixture has stood 24 hrs., filter off the cis-salt, wash it with acid-free alcohol, and dry it in air. The yield is 10·7 grms.

E. Biilmann and A. C. Anderson recommended reducing a soln. of ammonium chloroplatinate to chloroplatinite by ammonium oxalate, treating the filtered liquid with $5N$-NH_4OH, allowing the mixture to stand 24 hrs. at 0°, and crystallizing the cis-salt from boiling, 4 per cent. hydrochloric acid. F. Hoffmann, P. Klason,

and L. Ramberg employed modifications of this process. P. Klason also obtained the cis-salt by adding ammonia to a cold, aq. soln. of potassium amminotrichloroplatinite; J. Thomsen, by converting the copper in cuprous tetramminochloroplatinite into sulphide by means of hydrogen sulphide, warming the alkaline filtrate whereby a black substance is precipitated; the yellow liquor is then evaporated and cooled. H. and A. Euler obtained the salt along with $Pt_2(NH_3)_4Cl_2$ in their study of the action of ammonia on hydrochloroplatinous acid; and W. Lossen found that it is formed among the products of the action of hydroxylamine hydrochloride on platinic chloride. The compound was studied by A. Grünberg and D. I. Rjabtschikoff.

The cis-salt furnishes yellow, or dark yellow acicular or prismatic crystals. H. D. K. Drew and co-workers said that the colour is a deeper yellow than is the case with the α-salt; the crystals are mostly acicular; with a straight extinction—frequently inclined; positive elongation; twinning is common but different from that of the α-salt. The refractive index is about 1·76. A. M. Boldyreva said that the crystals are tetragonal. M. Peyrone found that the salt decomposes at 270° with the evolution of ammonium and hydrogen chlorides. The electrical conductivity of a rapidly prepared soln. of a mol of the salt in 1000 litres of water is nearly zero, being about 1·17. The conductivity, or ionization, increases with time. Thus, S. M. Jörgensen reported that the mol. conductivity of a soln. of a mol of the salt in 1000 litres of water at 25° is :

Time . . .	0	15	25	45	90 minutes
μ	5·4	8·6	9·2	12·8	20·8

A. Werner and A. Miolati, and A. Werner and C. Herty discussed this subject. W. Odling said that the salt is soluble in water, and, added M. Peyrone, without change, but P. Klason found that at 100°, the cis-salt slowly passes into the trans-salt, and that the change is faster at a higher temp. L. Tschugaeff and I. Tscherniaeff oxidized Peyrone's salt with ammonium persulphate and obtained $PtCl_2(OH)(NH_3)_2$. M. Peyrone found that 1 part of the salt dissolves in 33 parts of boiling water; P. T. Cleve said 26 parts of boiling water, and 387 parts of water at 0°; and P. Klason said 390 parts of water at ordinary temp. H. D. K. Drew and co-workers found that 100 grms. of water at 25° dissolve 0·2523 grm. of the β-salt. H. D. K. Drew and co-workers found the mol. conductivities of soln. with a mol of the β-salt in 1234 litres to be respectively 7·7, 14·4, 36·8, and 86·0 for times 0, 66, 193, and 1397 min.; and they attributed the change to the generation of ammonium chloride by the disruptive action of water. L. Tschugaeff and W. Chlopin observed that hydrogen dioxide converts Peyrone's chloride into platinic dichlorodihydroxydiammine, ozone in hydrochloric acid soln. increases the valency of Peyrone's chloride, but adds two chlorine atoms; in alkaline soln., both addition and substitution may occur simultaneously. P. T. Cleve observed that chlorine, or aqua regia forms hexagonal or rhombic plates of cis-$[Pt(NH_3)_2Cl_4]$; M. Peyrone, that hydrochloric acid dissolves it without decomposition; P. T. Cleve, that sulphur dioxide passed into a boiling soln. forms cis-$[Pt(NH_3)_2(HSO_3)Cl]$, and sodium sulphite forms $3Na_2SO_3.PtSO_3.1\frac{1}{2}H_2O$; M. Peyrone, that dil. sulphuric acid dissolves the salt without decomposition, that the cold, conc. acid has no action, but the hot, conc. acid decomposes it with the evolution of hydrogen chloride and sulphur dioxide. L. Tschugaeff and W. Chlopin observed that Peyrone's chloride is acted on by ammonia and ammonium carbonate to form platinic hydroxypentamminocarbonate—*vide supra*, the trans-salt. M. Peyrone found that nitric acid transforms the Peyrone's chloride without the separation of platinum into lemon-yellow octahedra; and P. T. Cleve, that boiling with aq. ammonia converts the salt into platinous tetramminechloride, whilst boiling alkali-lye forms $Pt_2(NH_3)_4(OH)_2H_2O$. L. Ramberg studied the evolution of ammonia from the platinum ammines boiled with alkali-lye. M. Peyrone observed that a soln. of ammonium carbonate converts the

cis-salt into the tetramminochloride, but an aq. soln. of potassium carbonate dissolves the cis-salt with difficulty, and without chemical change. P. T. Cleve observed that an excess of a soln. of potassium cyanide forms potassium cyanidoplatinate with the evolution of ammonia. M. Peyrone observed that with silver nitrate, silver chloride is precipitated, and P. T. Cleve added that the corresponding cis-salt is formed, thus, with silver nitrate there is produced *cis*-$[Pt(NH_3)_2(NO_3)_2]$. P. Klason observed that with mercaptan, $[Pt(NH_3)_2Cl(C_2H_5S)]$ is formed.

C. W. Blomstrand, and P. T. Cleve represented the α- and β-salts:

Trans- or α-salt	Cis- or β-salt
$\mathrm{Pt}{<}^{NH_3Cl}_{NH_3Cl}$	$\mathrm{Pt}{<}^{NH_3.NH_3Cl}_{Cl}$

and S. M. Jörgensen at first accepted these formulæ, but finally reversed them. The subject was discussed by F. Rosenblatt and A. Schleede, F. G. Angell and co-workers, H. Reihlen and G. von Hühn, H. D. K. Drew and F. S. H. Head, and F. P. J. Dwyer and D. P. Mellor. P. Klason represented the salts by the formulæ:

$$\mathrm{Pt}{<}^{NH_3Cl}_{NH_3Cl} \qquad\qquad H_3N{=}\mathrm{Pt}{<}^{NH_3Cl}_{Cl}$$

and A. Werner used the planar formulæ, now generally accepted, namely:

$$\begin{matrix}H_3N\\Cl\end{matrix}{>}\mathrm{Pt}{<}\begin{matrix}Cl\\NH_3\end{matrix} \qquad\qquad \begin{matrix}H_3N\\H_3N\end{matrix}{>}\mathrm{Pt}{<}\begin{matrix}Cl\\Cl\end{matrix}$$

The subject was discussed by H. Reihlen and K. T. Nestle, A. Grünberg, A. Cossa, A. Rosenheim and W. Händler, and F. W. Pinkard and co-workers. H. D. K. Drew and co-workers found that when the α-salt is treated with alkali hydroxides, or silver oxide, a base is formed, which, when neutralized with hydrochloric acid, forms a third isomeride, **platinous γ-dichlorodiammine,** $[Pt(NH_3)_2Cl_2]$, with a calculated mol. wt. of 300. Mol. wt. determinations by the b.p. of aq. soln. are in agreement with this degree of complexity for the β- and γ-salts, but the results with the α-salt are less decisive. If this isomeride really exists, and the observations of K. A. Jensen make it very doubtful, it shows that A. Werner's planar formulæ are not a complete explanation of the isomerism of the dichlorodiammines unless it be assumed that the four linkages to the platinum are inclined at fixed angles which are not right angles. This hypothesis is improbable. H. D. K. Drew and co-workers also showed that evidence does not favour the existence of planar and tetrahedral types, or of spatial and structural types, but rather supports the assumption that the three dichlorodiammines are structural isomerides:

α-Salt	β-Salt	γ-Salt
$\begin{matrix}H_3N\searrow\\Cl\nearrow\end{matrix}\mathrm{Pt}\begin{matrix}\swarrow NH_3\\ \nwarrow Cl\end{matrix}$	$\begin{matrix}ClH_3N\\ClH_3N\end{matrix}{>}\mathrm{Pt}$	$\begin{matrix}H_3N\searrow\\Cl\nearrow\end{matrix}\mathrm{Pt}{/}NH_3Cl$

The β-salt gives an intense purple coloration when rubbed with phenoxtellurine dibisulphate, but not so with the α- and γ-salts, the reaction is analogous with the behaviour of tellurides, selenides, and sulphides observed by H. D. K. Drew, and hence it is assumed that the β-salt has a formula of the type PtX_2. The colorations produced by the tri- and tetra-ammines depend on the presence of a salt of this type when the salt is in equilibrium—*e.g.* $[Pt(NH_3)_4]PtCl_4 \rightleftharpoons [Pt(NH_3)_4]Cl_2 + PtCl_2$; and the chloroplatinites: $K_2PtCl_4 \rightleftharpoons 2KCl + PtCl_2$. Derivatives of quadrivalent platinum do not give this coloration; and this is also the case with ordinary platinous chloride which shows that this salt does not possess the simple structure.

The reaction of the dichlorodiammines with silver oxide is slow, but it proceeds more rapidly with warm soln. The β-salt gives a soluble, hygroscopic yellow base, but the α-isomeride produces the same base as the γ-isomeride. The product is

assumed to be the base of the γ-salt because it yields the γ-salt when neutralized by hydrochloric acid, and the change from the α- to the γ-form is symbolized :

$$\begin{matrix} H_3N \searrow \\ Cl \nearrow \end{matrix} Pt \begin{matrix} \swarrow NH_3 \\ \nwarrow Cl \end{matrix} \rightarrow \begin{matrix} H_3N \searrow \\ Cl \nearrow \end{matrix} Pt \begin{matrix} \swarrow NH_2 \\ \end{matrix} \rightarrow \begin{matrix} H_3N \searrow \\ HO \nearrow \end{matrix} Pt \begin{matrix} \diagup NH_3.OH \\ \end{matrix}$$

In the dipyridine series where no hydrogen is attached to nitrogen, no γ-base is formed, since the β-chloro-salt forms $Pt(py.OH)_2$, and the α-salt, the α-base, $[Pt\,py_2(OH)_2]$. The action of an aq. soln. of potassium or sodium hydroxide on the three dichlorodiammines, resembles that of silver oxide, only the β-base is further changed by hot alkali-lye. The α- and β-dichlorodipyridines do not react appreciably with alkali-lye. The fact that β-dichlorodiammine cannot be obtained from tertiary aliphatic ammines, since only platinous chloride and a hydrochloride of the amine are formed, is in agreement with the assumption that the β-isomeride has the halogen attached to nitrogen, and the tendency to ionization is feeble.

When the dichlorodiammines are chlorinated, the α- and β-dichlorides unite each with two chlorine atoms to form the α- and β-tetrachlorides, which are not intertransformable ; the α-tetrachloride is tetragonal ; the β-tetrachloride, monoclinic or orthorhombic. The γ-dichloride gives on chlorination the α-tetrachloride. Each of the tetrachlorides gives back on reduction the particular dichloride from which it was originally formed ; it follows, therefore, that if the α- and the β-dichlorides are structural isomerides, the tetrachlorides are structural isomerides also. This is in agreement with the formulæ :

$$\begin{matrix} & Cl & \\ H_3N \searrow & \dot{Pt} & \swarrow NH_3 \\ Cl \nearrow & \cdot & \nwarrow Cl \\ & Cl & \end{matrix} \qquad\qquad \begin{matrix} ClH_3N \\ ClH_3N \end{matrix} > Pt < \begin{matrix} Cl \\ Cl \end{matrix}$$

α-Tetrachlorodiammine $\qquad$ β-Tetrachlorodiammine

According to H. D. K. Drew and co-workers, the crystals of γ-dichlorodiammine are orange-yellow, and mostly acicular, with a tendency to parallel growths and dendritic forms ; radiated growths occur. The extinction is straight, and the elongation negative. The refractive index is less than is the case with the α- or β-salts. The X-radiograms are different from those of the α-salt. The mol. conductivities, μ, for soln. with $v=4690$, and 1234 litres per mol, were very low at the start, but they rapidly increase with time owing to the generation of ammonium chloride, and not to hydrolysis, or to the catalytic effect of the platinized electrodes :

Time	0	67	139	1410
μ $v=4690$	21·3	30·3	56·0	116·6
μ $v=1234$	5·6	7·9	14·7	30·7

At 25°, 100 grms. of water dissolve 0·0491 grm. of the γ-salt. For some reactions of the salt, *vide supra*. F. Rosenblatt and A. Schleede concluded from the X-radiograms that the γ-salt is another crystalline form of the *trans*-salt. H. D. K. Drew and F. S. H. Head prepared a representative of the cis- and trans-isomerides of the platinous tetrammines : $[Pt(NH_3)(C_2H_5.NH_2)\{NH_2.CH_2.C(CH_3)_2.NH_2\}]Cl_2$; and A. Hantzsch, those of pyridine.

C. W. Blomstrand, and P. Klason added the theoretical amount of hydrochloroplatinic acid to a soln. of potassium trichloroamminoplatinite, and on evaporating the soln. in a current of air at ordinary temp. until no hydrotrichloroamminoplatinous acid remains, and washing out the potassium chloroplatinite with cold water, there is formed a yellowish-brown, crystalline powder of **platinous dichloroammine,** $[Pt(NH_3)Cl_2]_2$, which remains unchanged at 108° ; it is almost insoluble in cold water, and not very soluble in hot water ; the compound is hydrolyzed so that the evaporation of aq. soln. is conducted at ordinary temp. and in vacuo.

E. Koefoed prepared **platinous trichlorotriammine,** $Pt(NH_3)_3Cl_3$, by heating

platinous nitrosodichlorodiamminohydrochloride, $Pt(NH_3)_2Cl_2.NO.HCl$, at the temp. of boiling naphthalene until a soln. of the product in soda-lye gives no green precipitate with hydrochloric acid. The greyish-yellow product is not attacked by cold water, but it is attacked by hot water. The soln. in boiling water deposits on cooling platinous *cis*-dichlorodiammine, and hydrochloric acid added to the filtrate precipitates platinic dichlorotetramminochloride. Silver nitrate removes half the combined chlorine as silver chloride. The product may be a mixture of *cis*-$[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_4Cl_2]Cl_2$. L. Tschugaeff and I. Tscherniaeff prepared **platinous dichlorohydroxydiammine,** $PtCl_2(OH)(NH_3)_2$, by oxidizing Peyrone's salt with ammonium persulphate; by the cautious reduction of $PtCl_2(OH)_2(NH_3)_2$ with zinc dust; or by heating a mixture of $PtCl_2(NH_2)_2$ and $PtCl_2(OH)_2(NH_3)_2$ with slightly acidulated water.

P. Klason [7] regarded **trichloroamminoplatinous acid,** $H[Pt(NH_3)Cl_3].H_2O$, as the parent of a series of trichloroamminoplatinites. S. M. Jörgensen prepared **ammonium amminotrichloroplatinite,** $NH_4[Pt(NH_3)Cl_3].H_2O$, by treating the platinous tetramminochloride with ammonium chloroplatinite, filtering off the platinous tetramminochloroplatinite, concentrating the soln. on a water-bath until crystals of platinous *cis*-dichlorodiammine appear, and evaporating the filtered soln. in the cold over conc. sulphuric acid. P. Klason obtained it by heating platinous *cis*-dichlorodiammine with N-HCl on a water-bath, precipitating the hydrochloroplatinous acid by adding the theoretical quantity of platinous tetramminochloride, evaporating the soln. to dryness, in vacuo, and recrystallizing the product from the aq. soln. According to S. M. Jörgensen, the salt furnishes orange-red, rhombic bipyramidal crystals resembling those of the potassium salt. They effloresce and slowly lose their water over conc. sulphuric acid; they are rehydrated over water, and dehydrated at 98°. The aq. soln. furnishes crystals of platinous tetramminochloride, and of platinous trichloroammino-tetrammino-platinite, $[Pt(NH_3)Cl_3]_2[Pt(NH_3)_4]$, and the reaction is almost quantitative. When the salt is treated with mercaptan, P. Klason obtained platinous bissulphinoammine, $[Pt(NH_3\{(C_2H_5)_2S\}_2]_2$; and also a derivative of platinous chlorosulphinoammine, namely, $4[Pt(NH_3)Cl\{(C_2H_5)_2S\}][Pt(NH_3)Cl_2]$. The salt forms complexes: $[Pt(NH_3)Cl_3]_2[Pt(NH_3)_4]$; $[Pt(NH_3)Cl_3]_2[Pt(C_2H_5NH_2)_4]$; and $[Pt(NH_3)Cl_3]_2$-$[Pt(C_5H_5N)_4]$. H. Ley and K. Ficken prepared **potassium dichloroalaninoplatinite,** $K[Pt(C_3H_6O_2N)Cl_2]$, and also **potassium dichloroglycineplatinite,** $K[(PtC_2H_4O_2N)Cl_2]$.

A. Cossa prepared **potassium amminotrichloroplatinite,** $K[Pt(NH_3)Cl_3].H_2O$, by the action of ammonia on potassium chloroplatinite; and by the action of theoretical proportions of potassium chloroplatinite on $[Pt(NH_3)Cl_3]_2[Pt(NH_3)_4]$, and separating the $[Pt(NH_3)_4]PtCl_4$ simultaneously formed. The orange-red or reddish-yellow crystals, according to S. M. Jörgensen, are rhombic bipyramids with the axial ratios $a:b:c=1\cdot2620:1:0\cdot8231$. There is no marked cleavage. The optic axial angle $2V=64°$; the double refraction is negative; and the indices of refraction for Na-light are $\alpha=1\cdot5438$, and $\beta=1\cdot5754$. The pleochroism is: α, yellowish-red; β, reddish-yellow; and γ, deep yellow or red. The hardness is 1 to 2. A. Sella also made observations on the crystals. A. Cossa observed that when the salt is heated, it decomposes into platinum, potassium and ammonium chlorides, and hydrogen chloride. A. Werner and A. Miolati found the mol. conductivities of soln. of a mol of the salt in v litres of water, at 25°, to be:

v	125	250	500	1000	2000
μ	96·62	101·3	103·3	106·8	111·2

A. Cossa observed that the salt is soluble in water. It is transformed by chlorine, or a mixture of potassium permanganate and acid into platinum pentachloroammine; and warm hydrochloric acid forms ammonium chloride and potassium chloroplatinite. P. Klason observed that ammonia converts it into platinous *cis*-dichlorodiammine; and A. Cossa, that the reaction with ammonia proceeds through the stages $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_3Cl]Cl$, and $[Pt(NH_3)_4]Cl_2$. Alcohol

does not dissolve the salt, but with boiling alcohol, platinum is formed. A boiling soln. of sodium hydroxide does not split off ammonia, but it forms a black explosive product. S. M. Jörgensen, and A. Cossa prepared pale brown crystals of **silver amminotrichloroplatinite,** $Ag[Pt(NH_3)Cl_3]$, by the action of silver nitrate on the potassium salt. A. Cossa observed that an excess of silver nitrate in cold soln. of potassium amminotrichloroplatinite precipitates two-thirds of the chlorine as silver chloride, and with boiling soln., all the chlorine is precipitated. No sparingly-soluble complex salts are formed by potassium amminotrichloroplatinite with zinc, mercuric, or stannous chlorides. According to A. Werner, when an excess of a hot soln. of the potassium amminotrichloroplatinite is mixed with potassium amminopentachloroplatinite, a compound crystallizing in green leaflets is deposited at a certain temp., but is converted into potassium amminotrichloroplatinite as the mixture cools.

R. Uhlenhut [8] prepared **platinous tetrahydroxylaminechloride,** $[Pt(NH_4OH)_4]Cl_2$, by dissolving a gram of the hydroxide in 5 c.c. of boiling, dil. hydrochloric acid; W. Lossen, by warming a soln. of hydroxylamine hydrochloride with platinous chloride, concentrating by evaporation and cooling; and F. Hoffmann, by the action of an excess of hydroxylamine on platinous *cis*-dichlorobispyridine. H. Alexander made it by shaking platinous chloride with an excess of hydroxylamine, triturating the grey or brown product with cold hydrochloric acid, dissolving the mass in water, and precipitating with alcohol or with a current of hydrogen chloride; and also by mixing a 10 per cent. soln. of potassium chloroplatinite (1 mol.) with solid hydroxylamine hydrochloride (4 mols.), and then adding alkali carbonate. After the soln. has stood some time, add alkali-lye (2 mols.), dissolve the precipitate in the theoretical proportion of cold, dil. hydrochloric acid, and precipitate the salt from the filtered soln. by adding alcohol or passing hydrogen chloride through the liquid. The white, acicular or tabular crystals detonate when heated to about 110°. They are soluble in water and in ordinary alcohol, but, according to W. Lossen, insoluble in alcohol. H. Alexander, and R. Uhlenhut said that the salt is insoluble in conc. hydrochloric acid; hydrobromic acid gives colourless needles of the bromide; sodium thiosulphate gives a white crystalline precipitate; aq. ammonia, or alkali-lye precipitates the hydroxide; sodium carbonate or phosphate gives a fine crystalline precipitate; potassium chromate, a reddish-brown, amorphous precipitate; Fehling's soln., and auric chloride reduce the soln.; silver nitrate does not precipitate all the chloride; and platinic chloride or hydrochloroplatinic acid precipitates the **platinous tetrahydroxylaminechloroplatinate,** $[Pt(NH_2OH)_4]PtCl_4$, in blue or violet needles, which explode when heated above 100°. According to H. Alexander, the salt is insoluble in water but sparingly soluble in hot water; insoluble in alcohol; soluble in hydrochloric acid, and the yellow soln. on a water-bath furnishes the trans-salt $[Pt(NH_2OH)_2Cl_2]$; it dissolves with the development of red fumes in nitric acid; hydroxylamine converts it into platinous tetrahydroxylaminechloride; and a suspension of the salt in water when treated with ammonia forms a white precipitate.

According to H. Alexander, if the filtrate from the mixture of platinous chloride with an excess of hydroxylamine be evaporated at a low temp., and treated with alcohol, a white precipitate approximating **platinous tetrahydroxylaminehydroxychloride,** $[Pt(NH_2OH)_4](OH)Cl.2H_2O$, is formed; and **platinous tristetrahydroxylaminetetrahydroxydichloride,** $2[Pt(NH_2OH)_4](OH)_2.[Pt(NH_2OH)_4]Cl_2$, or $[Pt(NH_2OH)_4](OH)_2.2[Pt(NH_2OH)](OH)Cl$, is produced in microscopic needles by adding the theoretical proportion of barium oxide to a soln. of platinous chloride and hydroxylamine hydrochloride.

According to H. Alexander, if an excess of aq. ammonia be added to a soln. of platinous *trans*-dichlorodihydroxylamine, and the precipitate rapidly filtered off, washed with cold water, dissolved in a little cold hydrochloric acid, filtered, and mixed with conc. hydrochloric acid, with cooling, there is formed **platinous trans-dihydroxylaminediamminochloride,** $[Pt(NH_3)_2(NH_2OH)_2]Cl_2$; and the same product is obtained by dissolving the corresponding hydroxide in a little conc.

hydrochloric acid, and treating the soln. at a low temp. with alcohol. The colourless needle-like crystals are soluble in water, and insoluble in alcohol, or in conc. hydrochloric acid. Alkali hydroxides form a gelatinous precipitate of the dihydroxylaminediamminochloride; alkali carbonates, oxalates, and phosphates give white, crystalline precipitates; and potassium chloroplatinite, or hydrochloroplatinous acid, forms **platinous trans-dihydroxylaminediamminochloroplatinite,** $[Pt(NH_3)_2(NH_2OH)_2]PtCl_4$, in dark green, acicular crystals. L. Tschugaeff and I. I. Tscherniaeff could not confirm H. Alexander's observations on the action of ammonia on α-$Pt(NH_2OH)Cl_2$; and F. W. Pinkard and co-workers found that with a small proportion of aq. ammonia of sp. gr. 0·880, in the cold, the tetrammine, $[Pt(NH_2OH)_2(NH_3)_2](OH)_2$, is formed, but with dil. ammonia, a yellowish-brown precipitate of variable composition, is obtained, and which probably contains some $[Pt(NH_2OH)_2(NH_3)_2](OH)_2$. I. I. Tscherniaeff and A. S. Samsonova studied the subject.

F. Hoffmann, and L. Tschugaeff and I. I. Tscherniaeff also obtained **platinous** *cis*-**dihydroxylaminediamminochloride,** $[Pt(NH_3)_2(NH_2OH)_2]Cl_2$, by triturating platinous *cis*-dichlorodiammine with ten times its weight of water, adding the theoretical proportion of hydroxylamine hydrochloride, warming the mixture on a water-bath, then adding the theoretical amount of potassium carbonate dissolved in five times its weight of water, warming until solution is complete, and cooling. White, crystalline masses are formed. The salt is sparingly soluble in water, soluble in warm acids, and in acetic acid; it can be recovered unchanged by the evaporation of its soln. in hydrochloric or sulphuric acid. The aq. soln. is always turbid, and if the turbid soln. is clarified by animal charcoal, it slowly becomes turbid again at ordinary temp., and rapidly when heated. When treated with potassium chloroplatinite, violet crystals of **platinous** *cis*-**dihydroxylaminediamminochloroplatinite,** $[Pt(NH_3)_2(NH_2OH)_2]PtCl_4$, are formed, sparingly soluble in water and acids. L. Tschugaeff and I. I. Tscherniaeff also prepared **platinous dihydroxylaminodiamminochloropalladite,** $[Pt(NH_3)_2(NH_2OH)_2]PdCl_4$; **platinous trihydroxylaminoamminochloride,** $[Pt(NH_3)(NH_2OH)_3]Cl_2$; **platinous trihydroxylaminoamminochloroplatinite,** $[Pt(NH_3)(NH_2OH)_3]PtCl_4$; **platinous trihydroxylaminoamminochloropalladite,** $[Pt(NH_3)(NH_2OH)_3]PdCl_4$; **platinous hydroxylaminotriamminochloride,** $[Pt(NH_3)_3(NH_2OH)]Cl_2$; and **platinous hydroxylaminotriamminochloroplatinite,** $[Pt(NH_3)_3(NH_2OH)]PtCl_4$.

H. Alexander prepared **platinous** *trans*-**dichlorodihydroxylamine,** $[Pt(NH_2OH)_2]Cl_2$, by treating with warm hydrochloric acid the precipitate obtained by adding an excess of hydroxylamine to a soln. of platinous chloride; by evaporating on a water-bath the pale yellow soln. of platinous tetrahydroxylaminechloroplatinite, and cooling the liquor; and by digesting platinous tetrahydroxylaminechloride with an excess of hot hydrochloric acid and cooling—H. Wolfram employed a similar process. R. Uhlenhut obtained the salt by evaporating the filtrate, obtained in the preparation of platinous tetrahydroxylamine chloride, to about half its vol. and then cooling. The orange-yellow, or golden yellow, acicular crystals are less soluble in water than the tetrahydroxylaminechloride. They are soluble in alcohol, and in ether. The salt can be recrystallized from a soln. in dil. hydrochloric acid. Aq. ammonia forms the dihydroxylaminediamminochloride; and hydroxylamine, the tetrahydroxylaminechloride. Neither alkali hydroxides nor silver oxide produces the free base. When the soln. mixed with silver nitrate is allowed to stand for a long time in the cold, a feeble turbidity appears.

H. Wolfram prepared **platinous** *cis*-**dichlorodihydroxylamine,** $[Pt(NH_2OH)_2Cl_2]$, by mixing 2 c.c. of an 83 per cent. soln. of hydroxylamine with 2 c.c. of water, and adding the soln. to 11 grms. of potassium chloroplatinite dissolved in 50 c.c. of water; and F. Hoffmann, by mixing a mol. of potassium chloroplatinite in 100 c.c. of water with 2 mols. of hydroxylamine hydrochloride, and a mol. of potassium carbonate. The dark brown precipitate crystallizes after standing in contact with the mother-liquor for some hours.

F. Hoffmann, and L. Tschugaeff and I. I. Tscherniaeff prepared **platinous dichlorohydroxylaminoammine,** $[Pt(NH_3)(NH_2OH)Cl_2]$, by boiling in a flask with a reflux condenser, platinous *cis*-dihydroxylaminediamminochloride with sufficient dil. hydrochloric acid to dissolve the salt in the cold ; when the hot soln. is cooled, the salt separates in yellow crystals. L. Tschugaeff and I. I. Tscherniaeff reported **platinous hydroxychlorohydroxylamine,** $Pt(NH_2OH)Cl(OH)$, but F. W. Pinkard and co-workers could not confirm this.

L. Tschugaeff observed that complex hydrazine compounds can be prepared without difficulty if water be excluded, and he obtained **platinous tetrahydrazinochloride,** $[Pt(N_2H_4)_4]Cl_2$, by adding hydrazine to a soln. of platinous tripropylammoniumchloride $[Pt\{(C_3H_7)_3N.HCl\}_2Cl_2]$, in chloroform ; and L. Tschugaeff and M. Grigorieff prepared it by interaction of hydrazine hydrate with substances of the type $[Pt(SC_2H_5.C_2H_4.C_2H_5S)_2Cl_2]$, or of $[Pt(R_2S)_2Cl_2]$. The chloride can be kept for several days in the dry condition, but decomposes more rapidly in aq. soln. especially on the addition of alkali, with effervescence and liberation of platinum. With sodium iodide soln., the chloride gives a precipitate of the iodide, $[Pt(N_2H_4)_4]I_2$; whilst potassium platinochloride soln. produces a flesh-coloured precipitate. It forms **platinous tetrahydrazinochloroplatinite,** $[Pt(N_2H_4)_4]PtCl_4$; and **platinous tetrahydrazinohydrochloride.**

L. Tschugaeff and M. Grigorieff prepared **platinous trans-dihydrazinediamminochloride,** $[Pt(NH_3)_2(N_2H_4)_2]Cl_2$, by adding 4 to 6 c.c. of hydrazine hydrate to a gram of dry platinous *trans*-dichlorodiammine, the temp. rises a little, and as soon as all is dissolved an excess of alcohol is added. The oil which separates soon crystallizes, and the product is then washed with absolute alcohol, followed by dry ether. The product is dried a short time in air and finally over phosphorus pentachloride. The colourless acicular crystals are more stable and less soluble than the corresponding cis-salt. It gives a precipitate with potassium iodide ; and a red precipitate of **platinous dihydrazinodiamminochloroplatinite,** $[Pt(NH_3)_2(N_2H_4)_2]PtCl_4$, which soon darkens, is formed when the soln. is treated with potassium chloroplatinite. Hydrochloric acid in the cold forms a stable and sparingly soluble **platinous *trans*-dihydrazinediamminodihydrochloride,** $[Pt(NH_3)_2(N_2H_4)_2]Cl_2.2HCl$.

L. Tschugaeff and M. Grigorieff prepared **platinous *cis*-dihydrazinediamminochloride,** $[Pt(NH_3)_2(N_2H_4)_2]Cl_2$, by the action of hydrazine hydrate on platinous cis-dichlorodiammine, as in the case of the trans-salt. The cis-salt furnishes colourless, prismatic crystals, which can be preserved for a few days, but gradually darken owing to liberation of platinum ; the soln. in water, which dissolves large quantities of the solid, decomposes much more rapidly. The mol. conductivity of a soln. of a mol of the salt in 250 litres of water at 25° is 236·6. Other *salts* of the new complex were prepared by double decomposition of the chloride in concentrated aq. soln. with potassium iodide and with potassium platinochloride, the precipitate in the latter case being greenish. The addition of hydrochloric acid to an aq. soln. of the chloride causes the deposition of a much less soluble, crystalline **platinous *cis*-dihydrazinediamminodihydrochloride,** $[Pt(NH_3)_2(N_2H_4)_2]Cl_2.2HCl$, which, on treatment in aq. soln. with potassium chloroplatinite furnishes **platinous *cis*-dihydrazinediamminochloroplatinite,** $[Pt(NH_3)_2(N_2H_4)_2]_2(PtCl_4)_3$; and, on boiling with dil. hydrochloric acid yields hydrazine hydrochloride and platinous cis-dichlorodiammine. They also prepared **platinous dinitritodihydrazine,** $[Pt(N_2H_4)_2(NO_2)_2]$. L. Tschugaeff and co-workers prepared a series of **platinous hydrazinocarbylaminochlorides.**

Platinous chloride was found by A. Wurtz,[8] S. M. Jörgensen, and L. Tschugaeff to form a complex with methylamine, namely, **platinous quatermethylaminechloride,** $[Pt(CH_3NH_2)_4]Cl_2$, and the corresponding **platinous quaterethylaminochloroplatinite,** $[Pt(C_2H_5NH_2)_4]PtCl_4$. H. D. K. Drew and H. J. Tress obtained **platinous quaterethylaminochloride,** $[Pt\,etn_4]Cl_2.2H_2O$; **platinous quaterethylaminochloroplatinite,** $[Pt\,etn_4]PtCl_4$; **platinous dichloroquaterethylaminochloroaurate,** $[Pt\,etn_4Cl_2]AuCl_5$; and **platinous quaterpropylamino-**

chloride, [Pt pyn_4]$Cl_2.2H_2O$. S. M. Jörgensen prepared **platinous trans-bismethylaminediamminochloroplatinite,** $[Pt(NH_3)_2(CH_3NH_2)_2]PtCl_4$, as well as **platinous cis-bismethylaminediamminochloroplatinite.** D. Strömholm obtained complexes with mercuric chloride. A. Wurtz, C. Gordon, and S. M. Jörgensen obtained **platinous dichlorobismethylamine,** $[Pt(CH_3NH_2)_2Cl_2]$. S. M. Jörgensen prepared **platinous quaterdimethylaminechloride,** $[Pt\{(CH_3)_2NH\}_4]Cl_2$, **platinous quaterdimethylaminechloroplatinite,** $[Pt\{(CH_3)_2NH\}_4]PtCl_4$; **platinous dimethylaminetriamminochloride,** $[Pt(NH_3)_3\{(CH_3)_2NH\}]Cl_2$; **platinous dimethylaminetriamminochloroplatinite,** $[Pt(NH_3)_3\{(CH_3)_2NH\}]PtCl_4$; **platinous trans-bisdimethylaminediamminochloride,** $[Pt(NH_3)_2\{(CH_3)_2NH\}_2]Cl_2$; **platinous trans-bisdimethylaminediamminochloroplatinite,** $[Pt(NH_3)_2\{(CH_3)_2NH\}_2]PtCl_4$; S. M. Jörgensen, and E. Koefoed, **platinous cis-bisdimethylaminediamminochloride.** S. M. Jörgensen described two forms of $[Pta_2b_2]Cl_2$ in the case of platinic β-bisdimethylaminediamminochloride, $[Pt(NH_3)_2\{(CH_3)_2NH\}_2]Cl_2$, but H. D. K. Drew and G. H. Wyatt found that S. M. Jörgensen's products were impure and that there is only one form of this salt. S. M. Jörgensen also prepared **platinous cis-bisdimethylaminechloroplatinite**; and **platinous dichlorobisdimethylamine,** $[Pt\{(CH_3)_2NH\}_2Cl_2]$.

H. Wolffram, A. Wurtz, P. C. Ray and co-workers, L. Tschugaeff, J. Petersen, and A. Johnson studied **platinous quaterethylaminochloride,** $[Pt(C_2H_5NH_2)_4]Cl_2$, as a *white isomer*; and its *dihydrate*; and, by the action of a hydrochloric acid solution of hydrogen peroxide on this salt, H. Wolffram obtained what he considered to be a *red isomer* of the *dihydrate*; and also, **platinous quaterethylaminechloroplatinite,** $[Pt(C_2H_5NH_2)_4]PtCl_4$. H. Reihlen and E. Flohr found that **Wolffram's red salt** can also be prepared by mixing together aqueous solutions of colourless platinous quaterethylaminochloride and yellow platinic quaterethylaminochloride, [Pt etn_4Cl_2]Cl_2, and hence they concluded that Wolffram's red salt is probably a double salt, [Pt etn_4]Cl_2.[Pt etn_4Cl_2]$Cl_2.4H_2O$, because the red salt is pale yellow in aqueous solution, and gives with sodium chloroplatinate and potassium chloroplatinite products which correspond with the normal reactions of the components of the double salt. It is also assumed that when the red salt is dihydrated, the space-lattice is destroyed. It is not probable that the red colour of tho dihydrate is due to a special space-lattice because the dehydrated red salt changes from a yellow to a red colour, when re-hydrated by exposure to moist air.

H. Reihlen and E. Flohr said that the ionized halogen atoms of Wolffram's red salt cannot be replaced by radicles which would alter the space-lattice, but H. D. K. Drew and H. J. Tress pointed out that this statement merely refers to the difficulty involved in preparing these salts, and to differences in their stability. Two or four of the ethylamine groups may be replaced by propylamine groups; and a pale yellow **platinosic hydroxyquaterethylaminodichloride,** [Pt etn_4(OH)]$Cl_2.2H_2O$, can be prepared. This is taken to indicate that the red salt is possibly a **platinosic chloroquaterethylaminedichloride,** [Pt etn_4Cl]$Cl_2.CH_2O$, and that the special properties of Wolffram's salt are a consequence of chemical structure, and not of crystal space-lattice.

Whilst H. Reihlen and E. Flohr rejected the assumption that the platinum in the red salt is tervalent because "no compounds of tervalent platinum are known," on the contrary, several have been reported—*vide supra*. H. D. K. Drew and H. J. Tress considered the red salt to have tervalent platinum, [Pt etn_4Cl]$Cl_2.2H_2O$, in contrast with the intertransformable dimeric salt, [Cl etn_4Pt.Pt etn_4Cl]Cl_4, in which the platinum is quadrivalent. When the red salt is dissolved in water, one or other of these forms enters into equilibrium with the cations [Pt etn_4]$^{\cdot\cdot}$ and [Pt etn_4Cl_2]$^{\cdot\cdot}$ and Cl'-ions. K. A. Jensen said that it is doubtful if Wolffram's red salt contains tervalent platinum because it is diamagnetic, whereas the other compounds of tervalent platinum are paramagnetic.

P. C. Ray and P. C. Mukherjee prepared $[Pt(C_2H_5NH_2)_4]Cl_2.2H_2O$. A. Cossa described complexes with ammonia, $[Pt(C_2H_5NH_2)_4].[Pt(NH_3)Cl_3]_2$; with ethylamine, $[Pt(C_2H_5NH_2)_4][Pt(C_2H_5NH_2)Cl_3]_2$; and with pyridine, $[Pt(C_2H_5NH_2)_4][Pt(C_5H_5N(Cl_3]_2$. H. Reihlen and E. Flohr not only prepared the salt $[Pt(NH_2C_2H_5)_4]Cl_2.2H_2O$; but also the complex salts, $[Pt(NH_2C_2H_5)_4]Cl_2.Pt(NH_2C_2H_5)_4Cl_2]Cl_2.4H_2O$; $[Pt(NH_2C_2H_5)_2Cl_3]$; $[Pt(NH_2C_2H_5)_4]PtCl_2$; $[Pt(NH_2C_2H_5)_4Cl_2]PtCl_6$; and $[Pt(NH_2C_2H_5)_2]PtCl_4$. S. M. Jörgensen, J. Lifschitz and E. Rosenbohm, A. Hantzsch and F. Rosenblatt, P. T. Cleve, and C. Gordon prepared **platinous trans-bisethylaminediamminochloride,** $[Pt(NH_3)_2(C_2H_5NH_2)_2]Cl_2$, and also **platinous cis-bisethylaminediamminochloride,** and its *hemihydrate*, and also **platinous trans-bisethylaminediamminochloroplatinite,** $[Pt(NH_3)_2(C_2H_5NH_2)_2]PtCl_4$, and **platinous cis-bisethylaminediamminochloroplatinite.** S. M. Jörgensen prepared **platinous trans-bismethylaminebisethylaminechloride,** $[Pt(CH_3NH_2)_2(C_2H_5NH_2)_2]Cl_2$; **platinous trans-bismethylaminebisethylaminechloroplatinite,** $[Pt(CH_3NH_2)_2(C_2H_5NH_2)_2]PtCl_4$; **platinous cis-bismethylaminebisethylaminechloride**; and **platinous cis-bismethylaminebisethylaminechloroplatinite.** H. Wolffram obtained **platinous trans-dichlorobisethylamine,** $[Pt(C_2H_5NH_2)_2Cl_2]$, and S. M. Jörgensen, A. Wurtz, P. C. Ray and co-workers, C. Gordon, and H. Wolffram, **platinous cis-dichlorobisethylamine.** A. Cossa prepared impure **platinous dichloroethylamine,** $[Pt(C_2H_5NH_2)Cl_2]_2$. S. M. Jörgensen reported **platinous dichloroethylamineammine,** $[Pt(C_2H_5NH_2)(NH_3)Cl_2]$. P. Griess and C. A. Martius prepared **platinous dichloroethylenediethylamine,** $[Pt(C_2H_4)\{(C_2H_5)_2NH\}Cl_2]$. A. Cossa prepared **potassium ethylaminetrichloroplatinite,** $K[Pt(C_2H_5NH_2)Cl_3]$; **platinous tetramminoethyl-**

aminetrichloroplatinite, $[Pt(NH_3)_4][Pt(C_2H_5NH_2)Cl_3]$; and **platinous quinquiesethylaminetrichloroplatinite**, $[Pt(C_2H_5NH_2)_4][Pt(C_2H_5NH_2)Cl_3]$. S. M. Jörgensen, and J. Petersen described **platinous bisethylenediaminechloride**, $[Pt\{C_2H_4(NH_2)_2\}_2]Cl_2$, and **platinous bisethylenediaminechloroplatinite**, $[Pt\{C_2H_4(NH_2)_2\}_2]PtCl_4$—E. G. Cox and G. H. Preston studied the crystal lattices; and E. N. Gapon, the diffusion coeff., and N. S. Kurnakoff, **platinous bisethylenediaminechlorocobaltate**, $[Pt\{C_2H_4(NH_2)_2\}_2]CoCl_3$; and **platinous bisethylenediaminechlorocuprate**, $[Pt\{C_2H_4(NH_2)_2\}_2](CuCl_2)_2$, as well as **platinous bisethylenediaminechlorocupriplatinate**. S. M. Jörgensen, and P. Griess and C. A. Martius described **platinous trans-dichloroethylenediamine**, $[Pt\{C_2H_4(NH_2)_2\}Cl_2]$, and **platinous cis-dichloroethylenediamine**; **platinous ethylenediaminediamminochloride**, $[Pt(NH_3)_2\{C_2H_4(NH_2)_2\}]Cl_2$; S. M. Jörgensen, and H. D. K. Drew, **platinous ethylenediaminediamminochloroplatinite**, $[Pt(NH_3)_2\{C_2H_4(NH_2)_2\}]$-$PtCl_4$; and **platinous ethylenediaminediamminochloroplatinate**, $[Pt(NH_3)_2\{C_2H_4(NH_2)_2\}]PtCl_6$. S. M. Jörgensen, and P. Griess and C. A. Martius described **platinous tetrachloroethylenediaminebisethylene**, $[Pt_2\{C_2H_4(NH_2)_2\}(C_2H_4)_2Cl_4]$. S. M. Jörgensen, and V. von Lang described **platinous ethylenediaminedihydrochloride**, $C_2H_4(NH_2)_2.2HCl.PtCl_2$, and the *dihydrate*; S. M. Jörgensen, **platinous ethylenediaminehydrochloroplatinite**, $C_2H_4(NH_2)_2$.-$2HCl.PtCl_2.H_2PtCl_4$; and **platinous ethylenediamine ethylenediaminehexachloroplatinite**, $[Cl_3Pt\{C_2H_4(NH_2)_2\}PtCl_3]H_2\{C_2H_4(NH_2)_2\}$, and **ethylenediamine ethylenetrichloroplatinite**, $[Pt(C_2H_4)Cl_3]_2H_2\{C_2H_4(NH_2)_2\}$. H. Reihlen and W. Hühn prepared **platinous phenylethylenediaminochloride**, [Pt pen Cl_2]. F. G. Mann did not succeed in preparing **platinous dichlorodiaminodiethyleneaminohydrochloride**, $[Cl_2Pt(H_2N.C_2H_4)_2NH.HCl]$; but he did obtain the corresponding **platinous dichlorodiaminodiethyleneaminohydrochloridechloroplatinite**, $[Cl_2Pt(H_2N.C_2H_4)_2NH.HCl]_2PtCl_2.H_2O$, and also **platinous chlorodiaminodiethylaminomonochloride**, $[ClPt(H_2N.C_2H_4)_2NH]Cl$. W. H. Mills and T. H. H. Quibell resolved **platinous diphenyldimethyldiaminobisethylenediaminochloride**,

$$\left[\begin{matrix}CH_2.NH_2 \\ \vdots \\ C(CH_3)_2.NH_2\end{matrix}\!\!>Pt<\!\!\begin{matrix}NH_2.CH(C_6H_5) \\ \\ NH_2.CH(C_6H_5)\end{matrix}\right]Cl_2$$

into antimeric optically active forms which is taken to show that the 4-covalent platinum must have a planar configuration of its valencies, since the regular tetrahedral arrangement would have a symmetrical configuration for the complex cation.

L. A. Tschugaeff and B. Orelkin obtained **platinous bisaminoacetalchloride**, $[Pt\{NH_2.$-$CH_2.CH(OC_2H_5)_2\}_2]Cl_2$. P. Griess and C. A. Martius prepared **aniline ethylenetrichloroplatinite**, $[Pt(C_2H_4)Cl_3]H(C_6H_5NH_2)$; **ammonium ethylenetrichloroplatinite**, $NH_4[Pt(C_2H_4)Cl_3]$, as well as the *monohydrate*, and W. C. Zeise's *tetritapentahydrate*; W. C. Zeise, K. Birnbaum, J. von Liebig, and S. M. Jörgensen obtained **potassium ethylenetrichloroplatinite**, $K[Pt(C_2H_4)Cl_3]$, and the *monohydrate*; S. M. Jörgensen, **silver ethylenetrichloroplatinite**, $Ag[Pt(C_2H_4)Cl_3]$; **platinous tetramminoethylenedichloroplatinite**, $[Pt(NH_3)_4][Pt(C_2H_4)Cl_2]$; W. C. Zeise, and P. Griess and C. A. Martius reported **platinous dichloroethyleneammine**, $[Pt(NH_3)(C_2H_4)Cl_2]$; and P. Schützenberger and D. Tommasi, **platinous dichlorocarbonylethylene**, $[Pt(C_2H_4)(CO)Cl_2]$. W. C. Zeise, W. Prandtl and K. A. Hofmann, P. Klason, S. M. Jorgensen, J. von Liebig, and W. Prandtl and K. A. Hofmann, **platinous dichloroethylene**, $[Pt(C_2H_4)Cl_2]_2$. L. Tschugaeff and B. Orelkin prepared a complex with **aminoacetal**.

S. M. Jörgensen prepared **platinous quaterpropylaminochloride**, $[Pt(C_3H_7NH_2)_4]Cl_2$, and **platinous quaterpropylaminechloroplatinite**, $[Pt(C_3H_7NH_2)_4]PtCl_4$; **platinous cis-dichlorobispropylamine**, $[Pt(C_3H_7NH_2)_2Cl_2]$; **platinous trans-bispropylaminediamminochloroplatinite**, $[Pt(NH_3)_2(C_3H_7NH_2)_2]PtCl_4$, and **platinous cis-bispropylaminediamminochloroplatinite**; **platinous trans-bismethylaminebispropylaminechloroplatinite**, $[Pt(CH_3NH_2)_2(C_3H_7NH_2)_2]PtCl_4$, and **platinous cis-bismethylaminebispropylaminechloroplatinite**; **platinous trans-bisethylaminebispropylaminechloride**, $[Pt(C_2H_5NH_2)_2(C_3H_7NH_2)_2]Cl_2$; **platinous trans-bisethylaminebispropylaminechloroplatinite**, $[Pt(C_2H_5NH_2)_2(C_3H_7NH_2)_2]PtCl_4$; and **platinous cis-bisethylaminebispropylaminechloride**. L. Tschugaeff also prepared **platinous bis-tripropylaminehydrochloride**, $2\{(C_3H_7)_3N.HCl\}PtCl_2$; F. G. Mann, **platinous bis-$\alpha\beta\gamma$-triaminopropanochloride**, $[Pt\{NH_2.CH_2.CH(NH_2).CH_2.NH_2\}_2]Cl_2$, and **platinous dichlorohydrochloro-$\alpha\beta\gamma$-triaminopropane**, $[Pt\{NH_2.CH_2.CH(NH_2).CH_2.NH_2\}HCl.Cl_2]$. P. Pfeiffer and H. Hoyer studied the complexes with compounds having an ethylenic linkage. K. Birnbaum investigated **potassium propylenetrichloroplatinite**, $K[Pt(C_3H_6)Cl_3].H_2O$. G. Ponzio, **bis-iso-undecylaminechloroplatinite**, $(C_{11}H_{23}NH_3)_2PtCl_4$; A. Werner, A. Werner and C. H. Herty, and L. Tschugaeff and W. Sokoloff prepared **platinous cis-dichloropropylenediamine**, $Pt[\{C_3H_6(NH_2)_2\}Cl_2]$; and J. Ostromisslensky and A. Bergmann, L. Gerb, and A. Rosenheim and L. Gerb, **platinous cis-dichlorotoluylenediamine**, $[Pt\{C_6H_3.CH_3(NH_2)_2\}]Cl_2$. D. Strömholm obtained complexes with mercuric chloride. J. Weiss prepared **platinous trimethylaminetrichloroplatinite**, $[Pt\{(CH_3)_3N\}Cl_3]Cl$. P. C. Ray and co-workers prepared **platinous bisdiethylaminechloride**, $PtCl_2.2(C_2H_5)_2NH$, and a complex with acetone, $PtCl_2.2(C_2H_5)_2NH.(CH_3)_2CO$. P. C. Ray and co-workers prepared **platinous quaterbenzylaminechloride**, $PtCl_2(CH_2.C_6H_5.NH_2)_4$. F. G. Mann and W. J. Pope prepared **platinous dichloro-$\beta\beta'\beta''$-triaminotriethylaminochloroplatinite**, $2PtCl_2.N(C_2H_4.NH_2)_3$; and $3PtCl_2.2N(C_2H_4.NH_2)_3.6HCl.3H_2O$. A. Werner, and L. Tschugaeff and W. Sokoloff prepared **platinous bispropylenediaminechloride**, $[Pt\{C_3H_6)NH_2)_2\}_2]Cl_2$, as well as the *dextro-salt*, and the *lævo-salt*. A. Werner obtained

platinous propylenediaminodiamminochloride, $[Pt(NH_3)_2\{C_3H_5(NH_2)_2\}]Cl_2$; L. Tschugaeff and W. Sokoloff, the *lævo-salt*; A. Werner, **platinous propylenediaminediamminochloroplatinite,** $[Pt(NH_3)_2\{C_3H_5(NH_2)_2\}]PtCl_4$; L. Tschugaeff and W. Sokoloff, **platinous propylenediaminoethylenediaminechloride,** $[Pt\{C_2H_4(NH_2)_2\}\{C_3H_6(NH_2)_2\}]Cl_2$, and **platinous propylenediaminetrimethylenediaminechloride,** $[Pt\{C_3H_6(NH_2)_2\}\{(CH_2)_3(NH_2)_2\}]Cl_2$.

L. Tschugaeff, and C. Gordon prepared **platinous quaterbutylaminechloride,** $[Pt(C_4H_9NH_2)_4]Cl_2$, and **platinous quaterbutylaminechloroplatinite,** $[Pt(C_4H_9NH_2)_4]PtCl_4$; L. Tschugaeff obtained **platinous quaterisobutylaminechloroplatinite,** $[Pt(C_4H_9NH_2)_4]PtCl_4$; and C. Gordon, **platinous bisbutylaminediamminochloride,** $[Pt(NH_3)_2(C_4H_9NH_2)_2]Cl_2$. L. Tschugaeff reported **platinous quateramylaminechloroplatinite,** $[Pt(C_5H_{11}NH_2)_4]PtCl_4$; D. Strömholm obtained complexes with mercuric chloride; K. Birnbaum, **potassium amylenetrichloroplatinite,** $K[Pt(C_5H_{10})Cl_3].H_2O$; F. Mylius and F. Förster, **amylammonium carbonyltrichloroplatinite,** $[Pt(CO)Cl_3]H'(C_5H_{11}NH_2)$; and P. Schützenberger and D. Tommasi, **platinous chlorocarbonyldiamminochloride,** $[Pt(NH_3)_2(CO)Cl]Cl$. C. Liebermann and C. Paal prepared **allylaminetrichloroplatinous acid,** $[Pt(C_3H_5NH_2)Cl_3]H$; **ethylallylaminetrichloroplatinous acid,** $[Pt\{(C_2H_5)(C_2H_5)NH\}Cl_3]H$; **bisethylallylaminetrichloroplatinous acid,** $[Pt\{(C_2H_5)_2(C_3H_5)N\}Cl_3]H$; and **bispropylallylaminetrichloroplatinous acid,** $[Pt\{(C_3H_7)_2(C_3H_5)N\}Cl_3]H$. P. C. Ray and co-workers prepared **platinous quaterbenzylaminochloride,** $[Pt(CH_2.C_6H_5.NH_2)_4]Cl_2$. H. D. K. Drew and F. S. H. Head obtained various ammino-salts of ethylamine, *iso*butylenediamine, ethylenediamine, and pyridine. A. A. Grinberg prepared complexes with glycine, **platinous glycinodiamminochloride,** $Pt(NH_3)_2(C_2H_5O_2N)Cl$, and $Pt(NH_3)_2(C_2H_5O_2N).2HCl$.

M. Raowsky prepared **platinous quateranilinechloride,** $[Pt(C_6H_5NH_2)_4]Cl_2$; P. T. Cleve, **platinous trans-bisanilinediamminochloride,** $[Pt(C_6H_5NH_2)_2(NH_3)_2]Cl_2$; **platinous cis-bisanilinediamminochloride, platinous trans-bisanilinediamminochloroplatinite,** $[Pt(NH_3)_2(C_6H_5NH_2)_2]PtCl_4$, and **platinous cis-bisanilinediamminochloroplatinite.** J. J. Chydemus, C. Gordon, P. C. Ray and co-workers, D. Cochin, and P. T. Cleve described **platinous dichlorobisaniline,** $[Pt(C_6H_5NH_2)_2Cl_2]$; P. Griess and C. A. Martius, **platinous dichloroanilinethylene,** $[Pt(C_6H_5NH_2)(C_2H_4)Cl_2]$; F. Mylius and F. Forster, **aniline carbonyltrichloroplatinite,** $(C_6H_5NH_2)H[Pt(CO)Cl_3]$; and P. T. Cleve, **platinous chloroanilinediamminochloride,** $[Pt(NH_3)_2(C_6H_5NH_2)Cl]Cl$, and **platinous chloroanilinediamminochloroplatinite,** $[Pt(NH_3)_2(C_6H_5NH_2)Cl]_2PtCl_4$. P. C. Ray and co-workers, **platinous dichlorobisaniline,** $[Pt(C_6H_5NH_2)_2Cl_2]$; M. Raowsky prepared **platinous bisanilinehydrochloride,** $2C_6H_5NH_2.HCl.PtCl_2$, and the *pentahydrate.* P. C. Ray and co-workers prepared **platinous dichlorodimethylaniline,** $PtCl_2(CH_3)_2(C_6H_5)N$. C. Gordon, and D. Cochin prepared **platinous dichlorobistoluidine,** $[Pt(C_7H_7NH_2)_2Cl_2]$; and G. Gordon, **platinous dichlorobistolidine,** $[Pt(C_8H_9NH_2)_2Cl_2]$. F. Förster described **platinous dichlorocarbonylphenylhydrazine,** $[Pt\{C_6H_5N_2H_3\}(CO)Cl_2]$. P. Schützenberger, W. Manchot, A. J. F. da Silva, and W. Pullinger described **platinous dichlorodicarbonyl,** $[Pt(CO)_2Cl_2]$; W. Pullinger **platinous dichlorobischlorocarbonyl,** $[Pt(COCl_2)_2Cl_2]$; F. Mylius and F. Forster, W. Pullinger, P. Schützenberger, and A. J. F. da Silva, **platinous dichlorocarbonyl,** $[Pt(CO)Cl_2]_2$, and **platinous hemitricarbonylchloride,** $2PtCl_2.3CO$; and P. Schützenberger and D. Tommasi, **platinous chlorovinylcarbonyl,** $[Pt(CO)Cl(C_2H_3)]_2$.

E. Biilmann prepared **potassium allylalcoholotrichloroplatinite,** $K[Pt(C_3H_5OH)Cl_3]$; **cinchonine allylalcoholotrichloroplatinite,** $H_2(C_{19}H_{22}N_2O)[Pt(C_3H_5OH)Cl_3]_2$; and **platinous tetramminoallylalcoholotrichloroplatinite,** $[Pt(NH_3)_4][Pt(C_3H_5OH)Cl_3]_2$. F. W. Pinkard and co-workers prepared some complex pyridine salts—**platinous α-hydroxylaminopyridinechloride,** $[Pt(NH_2OH)\,py]Cl_2$; **platinous α-chlorobispyridinoamminochloride,** $[Pt(NH_3)\,py_2Cl]Cl$; **platinous α-chloropyridinodiamminochloride,** $[Pt(NH_3)\,py_2Cl]_2Cl$; **platinous α-chlorobispyridinoamminochloroplatinate,** $[Pt(NH)_3\,py_2Cl_2]PtCl_4$; **platinous α-hydroxylaminobispyridinoamminochloride,** $[Pt(NH_2OH)(NH_3)\,py_2]Cl_2$; **platinous α-hydroxylaminotrispyridinochloride,** $[Pt(NH_2OH)\,py_3]Cl_2$; **platinous α-dihydroxylaminobispyridinochloride,** $[Pt(NH_2OH)_2\,py_2]Cl$; and **platinous α-dihydroxylaminopyridinoamminochloride,** $[Pt(NH_2OH)_2(NH_3)\,py]Cl_2$. G. T. Morgan and F. H. Burstall prepared complexes with **dipyridyl.**

J. Peterson, S. M. Jörgensen, F. Förster, N. S. Kurnakoff, R. Lorenz and I. Posen, P. C. Ray and N. N. Ghosh, E. N. Gapon, A. Hantzsch and F. Rosenblatt, H. D. K. Drew and co-workers, P. C. Ray and co-workers, and S. G. Hedin described **platinous quaterpyridinechloride,** $[Pt(C_5H_5N)_4]Cl_2$, with the double salts **platinous quaterpyridinechlorocuprate,** $[Pt(C_5H_5N)_4](CuCl_3)_2$, and $[Pt(C_5H_5N)_4]_2CuCl_6.12H_2O$; **platinous quaterpyridinechlorozincate,** $[Pt(C_5H_5N)_4]ZnCl_4$; **platinous quaterpyridinechlorocadmate,** $[Pt(C_5H_5N)_4]CdCl_4$; **platinous quaterpyridinechlorocobaltate,** $[Pt(C_5H_5N)_4]CoCl_4$; **platinous quaterpyridinechloroplatinite,** $[Pt(C_5H_5N)_4]PtCl_4$; A. Cossa and S. G. Hedin, **platinous quaterpyridinechloroplatinate,** $[Pt(C_5H_5N)_4]PtCl_6$; A. Cossa, **platinous quaterpyridineamminotrichloroplatinite,** $[Pt(C_5H_5N)_4][Pt(NH_3)Cl_3]_2$; **platinous quaterpyridinoethylaminetrichloroplatinite,** $[Pt(C_5H_5N)_4][Pt(C_2H_5NH_2)Cl_3]_2$; and **platinous quinquiespyridinetrichloroplatinite,** $[Pt(C_5H_5N)_4][Pt(C_5H_5N)Cl_3]_2$. S. M. Jörgensen described **platinous pyridinetriamminochloride,** $[Pt(NH_3)_3(C_5H_5N)]Cl_2.H_2O$, and also **platinous pyridinetriamminochloroplatinite,** $[Pt(NH_3)_3(C_5H_5N)]PtCl_4$. E. N. Gapon, R. Lorenz and I. Posen, A. Hantsch and F. Rosenblatt, E. G. Cox, P. Klason, and S. M. Jörgensen prepared **platinous trans-bispyridinediamminochloride,** $[Pt(NH_3)_2(C_5H_5N)_2]Cl_2.H_2O$, and the corresponding

platinous cis-bispyridinediamminochloride, and **platinous trans-bispyridinediamminochloroplatinite**, $[Pt(NH_3)_2(C_5H_5N)_2]PtCl_4$, and the corresponding **platinous cis-bispyridinediamminochloroplatinite**. S. M. Jörgensen, and P. Klason prepared **platinous trans-dichloropyridineammine**, $[Pt(NH_3)(C_5H_5N)Cl_2]$, and the corresponding **platinous cis-dichloropyridineammine** —with a possible isomeric form of the latter. I. Ostromisslensky and A. Bergmann prepared **platinous chlorosulphitopyridinoammine**, $[Pt(NH_3)(C_5H_5N)(HSO_3)Cl]$; **platinous dichlorotolylenediamine**, $[Pt\{C_6H_3(CH_3)(NH_2)_2\}Cl_2]$; and **platinous dichloro-*iso*-butylenediamine**. C. W. Blomstrand, S. M. Jörgensen, H. Kirmreuther, F. Förster, P. C. Ray and co-workers, and S. G. Hedin reported **platinous trans-dichlorobispyridine**, $[Pt(C_5H_5N)_2Cl_2]$; and A. Cossa, **platinous dichlorobisypridine**. L. Tschugaeff and I. I. Tscherniaeff, I. I. Tscherniaeff and A. M. Rubinstein, and F. Hoffmann prepared **platinous bispyridinedihydroxylaminechloroplatinite**, $[Pt(NH_2OH)_2(C_5H_5N)_2]PtCl_4$; the corresponding **platinous hydroxybispyridinedihydroxylaminechloroplatinite**, $2[Pt(NH_2OH)_2(C_5H_5N)_2](OH)_2.3[Pt(NH_2OH)_2(C_5H_5N)_2]PtCl_4.8H_2O$; and **platinous dichlorohydroxylaminepyridine**, $[Pt(NH_2OH)(C_5H_5N)Cl_2]$. F. Förster obtained **platinous dichlorocarbonylpyridine**, $[Pt(C_5H_5N)(CO)Cl_2]$; S. M. Jörgensen, T. Anderson, A. Cossa, F. Hoffmann, S. G. Hedin, H. D. K. Drew and co-workers, and A. Werner and F. Fassbender, **platinous cis-dichlorobispyridine**; and F. Mylius and F. Förster, **pyridinium carbonyltrichloroplatinite**, $[Pt(CO)Cl_3]H(C_5H_5N)$, and a doubtful $2C_5H_5N.HCl.PtCl_2.CO$. S. M. Jörgensen described **platinous bispyridinehydrochloride**, $2C_5H_5N.HCl.PtCl_2$, or $[Pt(C_5H_5N)Cl_3]H(C_5H_5N)$; **platinous cis-bispyridinebisdimethyleneaminechloride**, $[Pt\{(CH_3)_2NH\}_2(C_5H_5N)_2]Cl_2$, **platinous cis-bispyridinebisdimethylaminechloroplatinite**, $[Pt\{(CH_3)_2NH\}_2(C_5H_5N)_2]PtCl_4$; **platinous trans-bispyridinebisethylaminechloroplatinite**, $[Pt(C_2H_5NH_2)_2(C_5H_5N)_2]PtCl_4$, and the corresponding **platinous cis-bispyridinebismethyldiaminechloroplatinite**. S. M. Jörgensen prepared **ammonium pyridinetrichloroplatinite**, $NH_4[Pt(C_5H_5N)Cl_3]$; A. Cossa, **pyridinium pyridinetrichloroplatinite**, $H(C_5H_5N)[Pt(C_5H_5N)Cl_3]$; A. Werner and F. Fassbender, and A. Cossa, **potassium pyridinetrichloroplatinite**, $K[Pt(C_5H_5N)Cl_3]$; A. Werner and F. Fassbender, **rubidium pyridinetrichloroplatinite**, $Rb[Pt(C_5H_5N)Cl_3]$; and **cæsium pyridinetrichloroplatinite**, $Cs[Pt(C_5H_5N)Cl_3]$; as well as **platinous tetrammine pyridinetrichloroplatinite**, $[Pt(NH_3)_4][Pt(C_5H_5N)Cl_4]_2$; **platinous quaterethylamine pyridinetrichloroplatinite**, $[Pt(C_2H_5NH_2)_4][Pt(C_5H_5N)Cl_3]_2$; and **platinous quaterpyridine pyridinetrichloroplatinite**, $[Pt(C_5H_5N)_4][Pt(C_5H_5N)Cl_3]_2$. P. C. Ray and P. C. Mukherjee prepared **platinous bispiperidinochloride**, $[Pt(C_5H_{11}N)_2]Cl_2.2H_2O$; and E. G. Cox and co-workers, **platinous disalicylaldoximinochloride**, $[Pt(C_7H_7O_2N)_2]Cl_2$.

G. Williams reported **platinous dichlorobispiperidine**, $[Pt(C_5H_{11}N)_2Cl_2]$; P. C. Ray and co-workers, $PtCl_2.3C_5H_{11}N$; A. Werner and F. Fassbender, **platinous dichloropiperidinepyridine**, $[Pt(C_5H_{11}N)(C_5H_5N)Cl_2]$; and G. Williams, and E. G. Cox and co-workers, **platinous dichlorobisquinoline**, $[Pt(C_9H_7N)_2Cl_2]$, also **platinous dichlorobisquinolinehydrochloride**, $2C_9H_7N.HCl.PtCl_2$; H. Reihlen and W. Hühn, with **3-methyl-2-aminomethyl-4-ethylquinoline chloroplatinite**, $[C_{13}H_{14}NH.NH_2]PtCl_4.4H_2O$; and $[Pt(C_{13}H_{14}N.NH_2)_2][PtCl_4]$. W. C. Zeise, and W. Prandtl and K. A. Hofmann prepared **platinous dichloromesityloxide**, $[Pt(C_6H_{10}O)Cl]$. F. Mylius and F. Förster described **quinoline carbonyltrichloroplatinite**, $[Pt(CO)Cl_3]H(C_9H_7N)$. A. Rosenheim and W. Händler obtained **platinous dichlorobis-2-amino-1-acetylpyridine**, $[Pt(C_7H_8ON_2)_2Cl_2]$; **platinous dichlorobis-3-aminopyridine**, $[Pt(C_5H_6N_2)_2Cl_2]$; **platinous dichloro-m-tolylenediamine**, $[Pt(C_7H_{10}N_2)Cl_2]$; and **platinous bis-m-tolylenediaminochloride**, $[Pt(C_7H_{10}N_2)_2]Cl_2$. K. A. Hofmann and J. von Narbutt prepared **platinous chloromethoxydi*cyclo*pentadiene**, $PtCl_2.C_{10}H_{12}.O(CH_3)$, and **platinous chloroethoxydi*cyclo*pentadiene**; L. Balbiano, **platinous dichlorobisdimethylethylpyrazole**, $PtCl_2\{C_3N_2(CH_3)_2(C_2H_5)\}_2$, and **platinous dichlorobismethylphenylpyrazole**. K. A. Hofmann and G. Büggo prepared **platinous dichlorobisacetonitrile**, $[Pt(CH_3.CN)_2Cl_2]$; **platinous dichlorobisphenylcarbylamine**, $[Pt(C_6H_5.NC)_2Cl_2]$; and **platinous dichlorobisbenzonitrile**. L. Tschugaeff and W. Lebedinsky obtained **platinous bisacetonitrilotetramminochloride**, $[Pt(NH_3)_4(CH_3.CN)_2]Cl_2$, in its isomeric forms, and chloroplatinites; they also prepared **platinous trichloroacetonitrilotetrammine**, $[PtCl_3(CH_3.CN)]_2[Pt(NH_3)_4]$, and **potassium trichloroacetonitrile**, $K[PtCl_3(CH_3.CN)]$. L. Tschugaeff and co-workers prepared **platinous quateraminoacetalchloride**, $[Pt\{NH_2.CH_2.CH(OC_2H_5)_2\}_4]Cl_2$; **platinous quateraminoacetalchloroplatinite**, $[Pt\{NH_2.CH_2.CH(OC_2H_5)_2\}_4]PtCl_4$; **platinous bisaminoacetaldiamminochloride**, $[Pt\{NH_2.CH_2.CH(OC_2H_5)_2\}_2(NH_3)_2]Cl_2$; and **platinous bisaminoacetaldiamminochloroplatinite**, $[Pt\{NH_2.CH_2.CH(OC_2H_5)_2\}_2(NH_3)_2]PtCl_4$; W. Prandtl and K. A. Hofmann obtained **platinous dichloroxymesityl**, $PtCl_2.C_6H_{10}O$; and E. G. Cox and co-workers, **platinous salicylaldoximechloride**, $[Pt(C_7H_7O_2N)_2Cl_2]$; and K. A. Jensen, **platinous dichloro compound**.

C. Enebuske described **platinous quatermethylsulphinechloride**, $[Pt\{(CH_3)_2S\}_4]Cl_2$; C. Enebuske, P. Klason, P. C. Ray and P. C. Mukherjee, E. G. Cox and co-workers, L. Tschugaeff and W. Sokoloff, and L. Tschugaeff and J. Benewolensky described **platinous quatermethylsulphinechloroplatinite**, $[Pt\{(CH_3)_2S\}_4]PtCl_4$, and **platinous quatermethylsulphinechloroplatinate**, $[Pt\{(CH_3)_2S\}_4]PtCl_6$; J. Petren, C. W. Blomstrand, and C. Enebuske, **platinous chlorotrismethylsulphinechloroplatinite**, $[Pt\{(CH_3)_2S\}_3Cl]PtCl_3$, or $[Pt\{(CH_3)_2S\}_2Cl_2][Pt\{(CH_3)_2S\}Cl_2]$. C. Enebuske, P. Klason, and L. Tschugaeff and J. Benewolensky described **platinous trans-dichlorobisdimethylsulphine**, $[Pt\{(CH_3)_2S\}_2Cl_2]$, and the corresponding **platinous cis-dichlorobisdimethylsulphine**, as well as the complex

with *chloroform*, described by C. Enebuske, and M. Weibull. P. Klason described **platinous bisdimethylsulphinediamminochloride**, $[Pt(NH_3)_2\{(CH_3)_2S\}_2]Cl_2$, and **platinous dimethylsulphinetriamminoehloride**, $[Pt(NH_3)_3\{(CH_3)_2S\}]Cl_2.H_2O$.

E. C. Fritzmann prepared **platinous quaterethylsulphinoehloride**, $[Pt\{(C_2H_5)_2S\}_4]Cl_2$; E. G. Cox and co-workers prepared salts of dimethylsulphine. The isomerism of these salts was discussed by F. G. Angell and co-workers. H. Löndahl prepared **platinous ehlorotrisdiethylsulphinechloride**, $[Pt\{(C_2H_5)_2S\}_3Cl]Cl$; C. W. Blomstrand, E. C. Fritzmann, and P. Klason, **platinous trans-dichlorobisdiethylsulphine**, $[Pt\{(C_2H_5)_2S\}_2Cl_2]$, as well as the corresponding **platinous cis-dichlorobisdiethylsulphine**, and the double salt with *platinous chloride*. P. C. Ray and P. C. Mukherjee prepared $Pt(C_2H_5)_2S.(C_2H_5)_2NH.Cl_2$; $(PtCl_2)_2.2(C_2H_5)_2S.(C_2H_5)_2NH$; $PtCl_2.(C_2H_5)_2S.(CH_3)_3N$. P. Klason, and L. Tschugaeff and N. Wladimiroff prepared **platinous dichlorodiethylsulphine**, $[Pt\{(C_2H_5)_2S\}_2Cl_2]_2$, as well as **platinous chloroethylmercaptidediethylsulphine**, $[Pt\{(C_2H_5)_2S\}_2Cl(C_2H_5S)]_2$, and **platinous diphenylsulphinediethylsulphine**, $[Pt\{(C_2H_5)_2S\}_2(SC_6H_5)_2]_2$. P. Klason reported **platinous chloromercaptammine**, $[Pt(NH_3)Cl(SC_2H_5)_2]_2$; and complexes with *platinous chloromercaptide*, $[Pt(NH_3)Cl(SC_2H_5)]_2.2PtCl(SC_2H_5)$; and with *platinous dichloroammine*, $[Pt(NH_3)Cl_2]_2.4[Pt(NH_3)Cl(SC_2H_5)_2.]$ H. D. K. Drew and G. H. Wyatt, P. Klason, and H. Löndahl obtained **platinous diethylsulphinetriamminochloride**, $[Pt(NH_3)_3\{(C_2H_5)_2S\}Cl_2$, in two isomeric forms, and also as a *monohydrate*, and **platinous diethylsulphinetriamminochloroplatinite**, $[Pt(NH_3)_3\{(C_2H_5)_2S\}]PtCl_4$. P. Klason prepared **platinous chlorodiethylsulphinediamminochloride**, $[Pt(NH_3)_2\{(C_2H_5)_2S\}Cl]Cl$, in two isomeric forms, as well as **platinous chlorodiethylsulphinediamminochloroplatinite**, $[Pt(NH_3)_2\{(C_2H_5)_2S\}Cl]_2PtCl_4$, and **platinous chlorodiethylsulphinediamminoethylmercaptide**, $[Pt(NH_3)_2\{(C_2H_5)_2S\}Cl]S(C_2H_5)$; **platinous trans-dichlorodiethylsulphinepyridine**, $[Pt(C_5H_5N)\{(C_2H_5)_2S\}Cl_2]$, and two isomeric forms of **platinous cis-diehlorodiethylsulphinepyridine**. P. C. Ray and co-workers prepared **platinous dichlorodiethylaminoethylsulphine**, $PtCl_2(C_2H_5)_2S.(C_2H_5)_2NH$, also $2PtCl_2.3(CH_3)_2S_2$, and $2PtCl_2.3(C_2H_5)_2S_2$. K. A. Jensen could not confirm the four isomers reported by P. C. Ray and K. C. Bose-Ray. K. A. Jensen measured the dipole moments of many of these salts, and also measured the electrical conductivities of solutions in water, and in methyl alcohol. Marked hydrolysis and alcoholysis occur. Molecular weight determinations correspond with the doubled formula $[PtCl_2(R_2S)_2]_2$. J. Lifschitz and W. Froentjes discussed the α- and β-forms of platinous bisdiethylsulphinedichlorides as structural isomerides. They obtained the α- and β-forms and a dimeric form of $[Pt\{(C_2H_5)(CH_3).S\}_2Cl_2]$, with the respective m.p. 63°, 127°, and 133°. They also obtained dextro- and lævo-forms with thiolactic acid. All the α-forms pass into the β-forms when exposed to ultra-violet light.

C. W. Blomstrand prepared **platinous dichlorodimethylsulphinediethylsulphine**, $[Pt\{(CH_3)_2S\}\{(C_2H_5)_2S\}Cl_2]$. H. Löndahl prepared **platinous bisdiethylenesulphinechloride**, $[Pt\{(C_2H_4)_2S_2\}_2]Cl_2$; **platinous dichlorodiethylenedisulphine**, $[Pt\{(C_2H_4)_2S_2\}Cl_2]$; **platinous chlorotrisdiethylenedisulphinechloride**, $[Pt\{(C_2H_4)_2S_2\}_3Cl]Cl$; and **platinous diethylenedisulphinetriamminochloride**, $[Pt(NH_3)_3\{(C_2H_4)_2S_2\}]Cl_2$. P. C. Ray and co-workers also prepared this compound.

P. C. Ray and P. C. Mukherjee, C. Rudelius, M. Weibull, and C. W. Blomstrand described **platinous quaterdipropylsulphinechloroplatinite**, $[Pt\{(C_3H_7)_2S\}_4]PtCl_4$; **platinous trans-dichlorobisdipropylsulphine**, $[Pt\{(C_3H_7)_2S\}_2Cl_2]$, and **platinous cis-dichlorobisdipropylsulphine**. There are also the double salts described by C. Rudelius, **platinous dichlorobisdipropylsulphinechloromercurate**, $[Pt\{(C_3H_7)_2S\}_2Cl_2]HgCl_2$, **platinous dichlorobisdipropylsulphinechlorostannite**, $[Pt\{(C_3H_7)_2S\}_2Cl_2]SnCl_2$, and **platinous dichlorobisdipropylsulphinechloroplatinite**, $[Pt\{(C_3H_7)_2S\}_2Cl_2]PtCl_2$. K. A. Jensen could not confirm C. Rudelius' α-$[PtCl_2\{(C_3H_3)_2S\}_2]$, but his γ-form was found to be the α-chloride. M. Weibull, and C. Rudelius prepared **platinous trans-dichlorobisdi-iso-propylsulphine**, $[Pt\{(C_3H_7)_2S\}_2Cl_2]$; C. Rudelius, **platinous chlorohydroxydipropylsulphine**, $[Pt\{(C_3H_7)_2S\}_2(OH)Cl]$; C. W. Blomstrand, and C. Rudelius, **platinous trans-dichlorodiethylsulphinedipropylsulphine**, $[Pt\{(C_2H_5)_2S\}\{(C_3H_7)_2S\}Cl_2]$; and H. Löndahl, **platinous dichlorodi-n-propylsulphinedi-iso-propylsulphine**, $[Pt\{(C_3H_7)_2S\}\{(C_3H_7)_2S\}Cl_2]$. E. C. Fritzmann described **platinous diethyldithiodimethylpropanochloride**, $2C(CH_3)_2(CH_2SC_2H_5)_2.2PtCl_2$; **platinous tetrathioerythritochloride**, $C(CH_2SC_2H_5)_4.PtCl_2$; **platinous dimethylethylenedithiolchloride**, $2(C_2H_5SHC : CHSC_2H_5)_2.PtCl_2$; and K. A. Jensen, **platinous thiocarbazidochloride**, $[Pt(thio)_2]Cl_2$, as well as **platinous thiocarbazidochloroplatinite**, $[Pt(thio)_2]PtCl_4$.

H. Löndahl, C. W. Blomstrand, and M. Weibull prepared **platinous quaterdi-n-butylsulphinechloroplatinite**, $[Pt\{(C_4H_9)_2S\}_4]PtCl_4$; **platinous quaterdi-iso-butylsulphinechloroplatinite**; **platinous trans-dichlorobisdi-n-butylsulphine**, $[Pt\{(C_4H_9)_2S\}_2Cl_2]$, and **platinous cis-dichlorobisdi-n-butylsulphine**; and similarly with **platinous trans-dichlorodi-isobutylsulphine**, and **platinous cis-diehlorodi-iso-butylsulphine**; H. Löndahl also prepared complexes with *carbon disulphide*, and with *chloroform*. K. A. Jensen could not confirm H. Löndahl's α- and γ-forms of $PtCl_2\{(C_4H_9)_2S\}_2$. H. Löndahl described **platinous trans-dichlorodiethylsulphinedibutylsulphine**, $[Pt\{(C_2H_5)_2S\}\{(C_4H_9)_2S\}Cl_2]$, and a complex with *chloroform*. C. W. Blomstrand prepared **platinous cis-diehlorobisdi-iso-amylsulphine**, $[Pt\{(C_5H_{11})_2S\}_2Cl_2]$; P. T. Cleve, **platinous trianilinediamminochloride**, $[Pt(NH_3)_2(C_6H_5NH_2)_3]Cl_2$; H. Löndahl, M. Weibull, and C. W. Blomstrand described **platinous trans-dichloro-**

bisdibenzylsulphine, $[Pt\{(C_5H_5CH_2)_2S\}_2Cl_2]$, and a complex with chloroform; and P. C. Ray and P. C. Mukherjee, a complex with ethylamine. P. C. Ray and co-workers prepared **platinous quaterbenzylsulphinochloride,** $PtCl_2.2(CH_2.C_6H_5)_2S$. L. Tschugaeff and S. Iljin prepared **platinous dichlorodimethyldimethyleneethylsulphine,** $PtCl_2.C(CH_3)_2(CH_2.SC_2H_5)_2$; **platinous dichloroerythritylethylsulphine,** $PtCl_2.C(CH_2.SC_2H_5)_4$; and **platinous dichloro-acetylenediethylsulphine,** $PtCl_2.S(C_2H_5).CH : CH.S(C_2H_5)$.

N. S. Kurnakoff, and W. J. Sell and T. H. Easterfield prepared **platinous quaterthio-carbamidochloride,** $[Pt\{CS(NH_2)_2\}_4]Cl_2$; and N. S. Kurnakoff, J. E. Reynolds, and G. Prätorius-Seidler, **platinous quaterthiocarbamidochloroplatinate,** $[Pt\{CS(NH_2)_2\}_4]PtCl_6$; N. S. Kurnakoff, **platinous bisthiocarbamidediamminochloride,** $[Pt(NH_3)_2\{CS(NH_2)_2\}_4]Cl_2$; **platinous dichlorobisthiocarbamide,** $[Pt\{CS(NH_2)_2\}_2Cl_2]$; **platinous dichlorothiocarbamide,** $[Pt\{CS(NH_2)_2\}Cl_2]_2$; J. E. Reynolds, G. Prätorius-Seidler, and B. Rathke, **platinous trichlorobisthiocarbamide,** $[Pt\{CS(NH_2)_2\}Cl_3]H\{CS(NH_2)_2\}$. N. S. Kurnakoff, **platinous quaterthioacetamidechloride,** $[Pt(CH_3.CS.NH_2)_4]Cl_2$, and **platinous quaterthioacetamidechloro-platinate,** $[Pt(CH_3.CS.NH_2)_4]PtCl_6$. A. W. Hofmann prepared **platinous thioformaldehyde-chloride,** $2PtCl_2.3C_3H_6S_3$; and K. A. Jensen, **platinous dichloro-β-aminodiethylsulphine,** $[Pt(C_2H_5SCH_2CH_2NH_2)Cl_2]$.

L. A. Tschugaeff and P. Teearu prepared **platinous quaterbutylcarbylaminechloride,** $[Pt(C_4H_9.NC)_4]Cl_2$; and **platinous quatermethylcarbylaminechloroplatinite,** $[Pt(CH_3.NC)_4]PtCl_4$; **platinous quaterbutylcarbylaminechloroplatinite,** $[Pt(C_4H_9.NC)_4]PtCl_4$; L. A. Tschugaeff and P. Teearu, **platinous dichlorobismethylcarbylamine,** $[Pt(CH_3.NC)_2Cl_2]$; **platinous dichloro-bisbutylcarbylamine,** $[Pt(C_4H_9.NC)_2Cl_2]$; L. Ramberg, L. Tschugaeff and P. Teearu, and K. A. Hofmann and G. Bügge, **platinous dichlorobisphenylcyanide,** $[Pt(C_6H_5.CN)_2Cl_2]$, and also associated with *chloroform,* and with benzene; **platinous dichlorobisphenylcarbylamine,** $[Pt(C_6H_5.NC)_2Cl_2]$, in a colourless and in a violet form; P. Klason, K. A. Hofmann and G. Bügge, L. Ramberg, C. Enebuske, and L. Tschugaeff and P. Teearu obtained **platinous quaterphenylcarbylaminechloroplatinite,** $[Pt(C_5H_5.NC)_4]PtCl_4$; L. A. Tschugaeff and co-workers prepared **platinous dihydrazinoctocarbylaminochloride,** $[(CH_3.CN)_4Pt(N_2H_3)_2Pt(CH_3.CN)_4]Cl_2.8H_2O$—*vide infra;* **platinous dihydrazinoctoethylcarbylaminochloride,** $[(C_2H_5.CN)_4Pt(N_2H_3)_2Pt(C_2H_5CN)_4]Cl_2$, and **platinous dihydroxoctoethylcarbylamminochloro-platinate,** $[(C_2H_5.CN)_4Pt(HO)_2Pt(C_2H_5.CN)_4]PtCl_6$; **platinous dihydrazinodihydrochlorotetra-carbylamminochloride,** $(CH_3.CN)_4Pt(N_2H_3)_2Pt2HCl.Cl_2$—*vide infra*—and **platinous dihydrazino-dihydrochlorotetraethylcarbylaminochloride,** $(C_2H_5.NC)_4Pt(N_2H_3)_2Pt2HCl.Cl_2$.

$$\left[\begin{matrix}CH_3NC \\ CH_3NC\end{matrix} \!>\! Pt \!<\! \begin{matrix}NH_2.NH \\ NH.NH_2\end{matrix} \!>\! Pt \!<\! \begin{matrix}CH_3NC \\ CH_3NC\end{matrix}\right]Cl_2 \quad \left[\begin{matrix}CH_3NC \\ CH_3NC\end{matrix} \!>\! Pt \!<\! \begin{matrix}NH_2.NH \\ NH.NH_2\end{matrix} \!>\! \overset{HCl}{\underset{HCl}{Pt}} \!<\! \begin{matrix}CH_3NC \\ CH_3NC\end{matrix}\right]Cl_2$$

P. C. Ray and N. N. Ghosh prepared $PtCl(C_2H_5)_2S_2$; $Pt_2Cl_2.(C_2H_5)_2S_2.2py$; and $Pt_3Cl_2.2(C_2H_5)_2S_2.2py$. L. Tschugaeff and B. Orelkin, **platinous quateramino-acetalchloride,** $[Pt\{(NH_2.CH_2CH(OC_2H_5)_2\}_4]Cl_2$; **platinous quateraminoacetalchloroplatinite,** $[Pt\{(NH_2.CH_2.CH(OC_2H_5)_2\}_4]PtCl_4$; L. Tschugaeff and B. Orelkin, **platinous bisamino-acetaldiamminochloride,** $[Pt(NH_3)_2\{NH_2.CH_2.CH(OC_2H_5)_2\}_2]Cl_2$, and **platinous bisaminoacetal-diamminochloroplatinite,** $[Pt(NH_3)_2\{NH_2.CH_2.CH(OC_2H_5)_2\}_2]PtCl_4$; and K. A. Hofmann and G. Bügge, **platinous dichlorodiacetonitrile,** $[Pt(CH_3.CN)_2Cl_2]$.

L. Tschugaeff and W. Chlopin, and L. Tschugaeff and A. Kobljansky prepared **platinous bisdimethyldithioethyleneglycolatochloroplatinite,** $[Pt(CH_3.S.C_2H_4.S.CH_3)_2]PtCl_4$; **platinous bisdiethyldithioethyleneglycolatochloride,** $[Pt(C_2H_5.S.C_2H_4.S.C_2H_5)_2]Cl_2$; **platinous bisdiethyldithioethyleneglycolatochloroplatinite,** $[Pt(C_2H_5.S.C_2H_4.S.C_2H_5)_2]PtCl_4$; **platinous bisdiethyldithioethyleneglycolatochloroplatinate,** $[Pt(C_2H_5.S.C_2H_4.S.C_2H_5)_2]PtCl_6$; **platinous bisdipropyldithioethyleneglyoolatochloroplatinite,** $[Pt(C_3H_7.S.C_2H_4.S.C_3H_7)_2]PtCl_4$; **platinous bisdibutyldithioethyleneglycolatochloroplatinite,** $[Pt(C_4H_9.S.C_2H_4.S.C_4H_9)_2]PtCl_4$; **platinous bis-diethyldithiopropyleneglycolatochloroplatinite,** $[Pt(C_2H_5.S.C_3H_6.S.C_2H_5)_2]PtCl_4$; **platinous bisdi-propyldithiopropyleneglycolatochloroplatinite,** $[Pt(C_3H_7.S.C_3H_5.S.C_3H_7)_2]PtCl_4$; and **platinous bisdiethyldithiohydroxyethyleneglycolatochloroplatinite,** $[Pt(C_2H_5.S.CH_2.CH(OH).CH_2.S.-C_2H_5)_2]PtCl_4$. L. Ramberg obtained a complex **platinous dichlorobisethylglycolatodiammine,** $3[Pt(NH_3)_2Cl_2].[Pt(NH_3)_2CO_2.CH_2.S.C_2H_5)]$. L. Ramberg prepared complexes containing ethylthioacetate, *e.g.*, **platinous dichlorodiamminobisethylthioacetate,** $Pt_2(NH_3)_4Cl_3(CO_2.CH_2.S.C_2H_5)(CO_2.CH_2.S.C_2H_5)$; and **monochlorobisethylthioacetoplatinous acid,** $PtCl(CO_2H.CH_2.S.C_2H_5)(CO_2.CH_2.S.C_2H_5)$. L. Tschugaeff and A. Kobljansky, **platinous dichloro-dithioethylenemethylglycolate,** $[Pt(CH_3.S.C_2H_4.S.CH_3)Cl_2]$: L. Tschugaeff and co-workers —W. Chlopin, W. Sokoloff, and A. Kobljansky—**platinous dichlorodithioethylene-ethylglycolate,** $[Pt(C_2H_5.S.C_2H_4.S.C_2H_5)Cl_2]$; **platinous dichlorodithioethylenepropylglycolate,** $[Pt(C_3H_7.S.C_2H_4.S.C_3H_7)Cl_2]$; **platinous dichlorodithioethylenebutylglyeolate,** $[Pt(C_4H_9.S.C_2H_4.S.C_4H_9)Cl_2]$; **platinous dichlorodithiopropyleneethylglycolate,** $[Pt(C_2H_3.S.C_2H_5.S.C_2H_5)]Cl_2$; **platinous dichlorodithiopropylenepropylglycolate,** $[Pt(C_3H_7.S.C_3H_6.S.C_2H_5)Cl_2]$; **platinous dichlorodithiooxytrimethyleneethylglycolate,** $[Pt(C_2H_3.S.CH_2.CH(OH).CH_2.S.C_2H_3)Cl_2]$; L. Ramberg, **platinous dichlorobisthioethylglycolate,** $[Pt(HOOC.CH_2.S.C_2H_5)_2Cl_2]$, in its

trans- and cis-forms; **platinous dichlorobismethylthioethylglycolate**, $[Pt(CH_3OOC.CH_2.S.C_2H_5)_2Cl_2]$, in its trans- and cis-forms; S. Tyden, **platinous dichlorobisthioglycolate**, $Pt[S(CH_2COOH)_2]_2Cl_2$; **platinous dichlorobisthiomethylglycolate**, $[Pt\{S(CH_2COOCH_3)_2\}_2Cl_2]$; **platinous dichlorobisthioethylglycolate**, $[Pt\{S(CH_2.COOC_2H_5)_2\}_2Cl_2]$; **platinous dichlorobisthiopotassiumglycolate**, $[Pt\{S(CH_2.COOK)_2\}_2Cl_2]$; **platinous dichlorobisthiobariumglycolate**; L. Ramberg and A. Tiberg, **platinous dichloroethylenethioglycolate**, $[PtC_2H_4\{S.CH_2(COOH)_2\}_2Cl_2]$; and **platinous dichloroethylenethiopotassiumglycolate**, $[Pt(C_2H_4\{S.CH_2(COOK)_2\}_2Cl_2]$; L. Ramberg, **platinous chloroethylthioglycolate**, $[Pt(HCO_2.CH_2.S.C_2H_5)(CO_2.CH_2.S.C_2H_5)Cl]$; S. Tyden, **platinous chlorodithioglycolate**, $[Pt\{S(CH_2.COOH)_2(HOCO.CH_2.S.CH_2.COO)\}Cl]$, and **platinous chlorodithiopotassiumdithioglycolate**, $[Pt\{S(CH_2.COOK)_2(KOCO.CH_2S.CH_2.COO)\}Cl]$. G. Wallin prepared **platinous dichlorodiamidoacetate**, $[Pt(NH_2.CH_2.COOH)_2Cl_2]$, and the dihydrate; **platinous dichlorodiaminomethylacetate**, $[Pt(NH_2.CH_2.COOCH_3)_2Cl_2]$; **platinous dichlorodiamidoethylacetate**, $[Pt(NH_2.CH_2.COOC_2H_5)_2Cl_2]$; H. Ley and K. Ficken, **potassium amidoacetatodichloroplatinite**, $K[Pt(NH_2.CH_2.CO_2)Cl_2]$; and **potassium amidopropionatodichloroplatinite**, $K[Pt(NH_2.CH_2.CH.CO_2)Cl_2]$. A. A. Grinberg, and A. A. Grinberg and B. V. Ptitzuin prepared compounds of the type of Peyronne's chloride with a mol. of $(H.COOH)_2$, or of glycine occupying two co-ordinated positions. L. Tschugaeff and B. Orelkin prepared **platinous dichlorodiamidoacetal**, $[Pt\{NH_2.CH_2.CH(OC_2H_5)_2\}_2Cl_2]$; E. G. Cox and co-workers, **platinous disalicylaldoximinochloride**. N. S. Kurnakoff, **platinous dichlorodithioacetamide**, $[Pt(CH_3.CS.NH_2)_2Cl_2]$, and **platinous bisthiocarbamidebispyridinechloride**, $[Pt(C_5H_5N)_2\{CS(NH_2)_2\}_2]Cl_2$. P. Klason prepared **platinous chloroethylmercaptidodiammine**, $[Pt(NH_3)_2Cl(SC_2H_5)]$; and **platinous chloroethylmercaptidodiamminochloroplatinite**, $[Pt(NH_3)_2Cl(SC_2H_5)]PtCl_2$; F Hoffmann, **platinous dichlorodiamminotrithiocarbonatodiammine**, $[Pt(NH_3)_2Cl_2][Pt(NH_3)_2(CS_3)]$.

N. S. Kurnakoff reported **platinous quatermonomethylthiocarbamidechloride**, $[Pt\{CS(NH_2)(NHCH_3)\}_4]Cl_2$; **platinous quatermonoethylthiocarbamidechloride**, $[Pt\{CS(NH_2)(NHC_2H_5)\}_4]Cl_2$; **platinous quatermono-iso-undecylthiocarbamidechloride**, $[Pt\{CS(NH_2)(NHC_{11}H_{23})\}_4]Cl_2$; **platinous quaterdiethylthiocarbamidechloride**, $[Pt\{CS(NHC_2H_5)_2\}_4]Cl_2$; **platinous quaterdi-iso-undecylthiocarbamidechloride**, $[Pt\{CS(NHC_{11}H_{23})_2\}_4]Cl_2$; **platinous quatertriethylthiocarbamidechloride**, $[Pt\{CS(NHC_2H_5)(N(C_2H_5)_2\}_4]Cl_2$; **platinous dichlorobistriethylthiocarbamide**, $Pt\{CS(NHC_2H_5)N(C_2H_5)_2\}_2Cl_2]$; **platinous quaterxanthogenamidechloride**, $[Pt(NH_2.CS.OC_2H_5)_4]Cl_2$, associated with *ethyl alcohol*; and H. Debus, and N. S Kurnakoff described **platinous quaterxanthogenamidechloroplatinate**, $[Pt(NH_2CS.OC_2H_5)_4]PtCl_6$; and G. Ponzio, **platinous dichlorobis-iso-undecylthiocarbamide**, $PtCl_2\{(CS)NH.C_{11}H_{23}\}_2$. J. Lifschitz and W. Froentjes prepared a series of **platinous thiolacetatochlorides**.

J. Petren, and E. C. Fritzmann studied **platinous quaterdiethylseleninechloride**, $[Pt\{(C_2H_5)_2Se\}_4]Cl_2$, **platinous quaterdiethylseleninechloroplatinite**, $[Pt\{(C_2H_5)_2Se\}_4]PtCl_4$; **platinous** ***trans*-dichlorobisdiethylselenine**, $[Pt\{(C_2H_5)_2Se\}_2Cl_2]$, **platinous** ***cis*-dichlorobisdiethylselenine**, and the salts **platinous dichlorobisdiethylseleninechloromercurate**, $[Pt\{(C_2H_5)_2Se\}_2Cl_2]HgCl_2$, and **platinous dichlorobisdiethylseleninechloroplatinite**, $[Pt\{(C_2H_5)_2Se\}_2Cl_2]PtCl_2$; **platinous** ***trans*-chloropyridinediethylselenine**, $[Pt(C_5H_5N)\{(C_2H_5)_2Se\}Cl_2]$; **platinous chlorotrisdiethylseleninechloroplatinite**, $[Pt\{(C_2H_5)_2Se\}_3Cl]PtCl_3$; and **platinous dichlorobisbenzyltellurine**, $PtCl_2.2(C_7H_7)_2Te$; **platinous trans-dichlorodiethylsulphinediethylselenine**, $[Pt\{(C_2H_5)_2S\}\{C_2H_5)_2Se\}Cl_2]$, **platinous cis-dichlorodiethylsulphinediethylselenine**, and **platinous dichlorodiethylsulphinediethylseleninechloroplatinite**, $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}PtCl_2]$; and E. C. Fritzmann, **platinous dichlorbisbenzyltelluride**, $[Pt\{(CH_2.C_6H_5)_2Te\}_2Cl_2]$.

A. Cahours and H. Gal prepared **platinous quatertrimethylphosphinechloride**, $[Pt\{P(CH_3)_3\}_4]Cl_2$; C. W. Blomstrand, H. Kolbe, and A. Cahours and H. Gal, **platinous** ***trans*-dichlorobistrimethylphosphine**, $[Pt\{P(CH_3)_3\}_2Cl_2]$, and **platinous** ***cis*-dichlorotrimethylphosphine**; A. Cahours and H. Gal, **platinous quatertriethylphosphinechloride**, $[Pt\{P(C_2H_5)_3\}_4]Cl_2$, **platinous quatertriethylphosphinechloroaurate**, $[Pt\{P(C_2H_5)_3\}_4](AuCl_4)_2$, and **platinous quatertriethylphosphinechloroplatinate**, $[Pt\{P(C_2H_5)_3\}_4]PtCl_6$. A. Werner, A. Sella, A. des Cloizeaux, P. T. Cleve, H. Kolbe, C. W. Blomstrand, and A. Cahours and H. Gal described **platinous trans-dichlorobistriethylphosphine**, $[Pt\{P(C_2H_5)_3\}_2Cl_2]$; and **platinous cis-dichlorobistriethylphosphine**. P. Klason and J. Wanselin, **platinous bistriethylphosphinediamminochloride**, $[Pt(NH_3)_2\}P(C_2H_5)_3\}_2]Cl_2$, and its two isomers, as well as **platinous bistriethylphosphinediamminochloroplatinite**, $[Pt(NH_3)_2\{P(C_2H_5)_3\}_2]PtCl_4$. K. A. Jensen measured the dipole moments of many of the *cis*- and *trans*-phosphino-compounds in addition to the platinous dichlorobistriethylphosphine—*e.g.* **platinous cis- and trans-dichlorobistripropylphosphine**, $[Pt\{(C_3H_7)_3P\}_2Cl_2]$; **platinous cis- and trans-dichlorobistributylphosphine**, $[Pt\{(C_4H_9)_3P\}_2Cl_2]$; and **platinous trans-dichlorobisphenyldiethylphosphine**, $[Pt\{(C_2H_5)_2(C_6H_5)P\}_2Cl_2]$.

A. Rosenheim and W. Levy prepared **platinous ethylphosphitochloride**, $PtCl_2.P(OC_2H_5)_3$; and P. Schützenberger and C. Fontaine prepared **platinous chloroethylphosphitotriamminochloroplatinite**, $[Pt(NH_3)_3\{P(OC_2H_5)_3\}Cl]PtCl_3$; and **platinous chloroethylphosphitotriamminochloroplatinate**, $[Pt(NH_3)_3\{P(OC_2H_5)_3\}Cl]PtCl_5$. P. Schützenberger, P. Schützenberger and C. Fontaine, and A. Rosenheim and W. Levy prepared **platinous bisethylphosphitodiamminochloride**, $[Pt(NH_3)_2\{P(OCH_3)_3\}_2]Cl_2$; D. Cochin, **platinous bisanilinebismethylphosphitochloride**, $[Pt(C_6H_5NH_2)_2\{P(OCH_3)_3\}_2]Cl_2$; **platinous bisanilinebisethylphosphitochloride**, $[Pt(C_6H_5NH_2)_2\{P(OC_2H_5)_3\}_2]Cl_2$; **platinous bistoluidinebismethylphosphito-**

chloride, $[Pt(C_7H_9NH_2)_2\{P(OCH_3)_3\}_2]Cl_2$; **platinous bistoluidinebisethylphosphitochloride,** $[Pt(C_7H_7NH_2)_2\{P(OC_2H_5)_3\}_2]Cl_2$; A. Rosenheim and W. Levy, P. Schützenberger, P. Schützenberger and C. Fontaine, and C. H. Herty and R. O. E. Davis, **platinous chloroethylphosphitodiamminochloride,** $[Pt(NH_3)_2\{P(OC_2H_5)_3\}Cl]Cl$; **platinous chloroethylphosphitodiamminochloroplatinate,** $[Pt(NH_3)_2\{P(OC_2H_5)_3\}Cl]PtCl_6$; and also complexes $[Pt(NH_3)_2\{P(OC_2H_5)_3\}]Cl_2$, or $[Pt(NH_3)_2\{P(OC_2H_5)_3\}]PtCl_6$; D. Cochin prepared **platinous chloroethylphosphitobisanilinochloride,** $[Pt(C_6H_5NH_2)_2\{P(OC_2H_5)_3\}Cl]Cl$; and **platinous chloroethylphosphitobistoluidinechloride,** $[Pt(C_7H_7NH_2)_2\{P(OC_2H_5)_3\}Cl]Cl$. A. Rosenheim and co-workers, and P. Schützenberger, **platinous dichlorobismethylphosphite,** $[Pt\{P(OCH_3)_3\}_2Cl_2]$; **platinous dichlorobisethylphosphite,** $[Pt\{P(OC_2H_5)_3\}_2Cl_2]$; A. Rosenheim and W. Levy, **platinous dichlorobisphenylphosphite,** $[Pt\{P(OC_6H_5)_3\}_2Cl_2]$; D. Cochin, **platinous dichloranilinemethylphosphite,** $[Pt(C_5H_5NH_2)\{P(OCH_3)_3\}Cl_2]$; D. Cochin, and A. Rosenheim and W. Levy, **platinous dichloroanilinethylphosphite,** $[Pt(C_6H_5NH_2)\{P(OC_2H_5)_3\}Cl_2]$, in its trans- and cis-forms; **platinous dichlorotoluidinemethylphosphite,** $[Pt(C_7H_7NH_2)\{P(OCH_3)_3\}Cl_2]$; P. Schützenberger and M. G. Saillard, M. G. Saillard, and G. Quesneville, **platinous dichlorotoluidinethylphosphite,** $[Pt(C_7H_7NH_2)\{P(OC_2H_5)_3\}Cl_2]$; in the trans- and cis-forms, and P. Schützenberger, **platinous chlorohydroxytoluidinethylphosphite,** $[Pt(C_7H_7NH_2)\text{-}\{P(OC_2H_5)_3\}(OH)Cl]$. A. Rosenheim and W. Levy prepared **platinous dichloropyridinethylphosphite,** $[Pt(C_5H_5N)\{P(OC_2H_5)_3\}Cl_2$, in its trans- and cis-forms; G. Quesneville, **platinous hydroxychlorophosphoanilidephosphoxyanilide,** $[Pt\{P(C_6H_6N)_3\}\{PO(C_6H_5N)\}(OH)Cl]$; **platinous hydroxychlorophosphoanilidephosphoxytoluidide,** $[Pt\{P(C_7H_8N)_3\}\{PO(C_7H_8N)\}(OH)Cl]$; P. Schützenberger and C. Fontaine, **platinous tetrachloroethylenebisethylphosphite,** $[Pt_2(C_2H_4)\{P(OC_2H_5)_3\}_2Cl_4]$; **platinous dichlorocarbonylethylphosphite,** $Pt(CO)\{P(OC_2H_5)_3\}Cl_2]$; **platinous dichlorophosphorustrioxidethylphosphite,** $[Pt\{P(OH)_3\}\{P(OC_2H_5)_3\}Cl_2$; **platinous dichlorophosphorustrichloridethylphosphite,** $[Pt(PCl_3)\{P(OC_2H_5)_3\}Cl_2]$; and **platinous dichloromethylphosphitoethylphosphite,** $[Pt\{P(OCH_3)_3\}\{P(OC_2H_5)_3\}]Cl_2$; P. Schützenberger and C. Fontaine, P. Schützenberger, and O. W. Gibbs, **platinous dichlorotrihydroxyphosphorous acid,** $[Pt\{P(OH)_3\}Cl_2]_2$; **platinous chlorooxypentahydroxyphosphite,** $[Pt\{P(OH)_3\}Cl\{OP(OH)_2\}]_2$; and **platinous chlorodioxytrihydroxyphosphite,** $[Pt\{P(OH)_3\}Cl(OPO)]_2$; P. Schützenberger, and C. Fontaine, **platinous dichloromethylphosphite,** $[Pt\{P(OCH_3)_3\}Cl_2]_2$; P. Schützenberger and C. Fontaine, and A. Rosenheim and W. Löwenstamm, **platinous dichloroethylphosphite,** $[Pt\{P(OC_2H_5)_3\}Cl_2]_2$; D. Cochin, **platinous dichloroethylphosphitechloroplatinite,** $[Pt\{P(OC_2H_5)_3\}Cl_2]_2.2PtCl_2$; E. Pomey, **platinous dichloropropylphosphite,** $[Pt\{P(OC_5H_7)_3\}\text{-}Cl_2]_2$; P. Schützenberger and C. Fontaine, **platinous dichloromonoallylphosphite,** $[Pt\{P(OH)_2\text{-}(OC_3H_5)\}Cl_2]_2$; **platinous dichlorodisilverphosphite,** $[Pt\{P(OH)(OAg)_2\}Cl_2]_2$, and some complex salts; **platinous dichlorotrisilverphosphite,** $[Pt\{P(OAg)_3\}Cl_2]_2$; and **platinous tetrachloroleadphosphite,** $[Pt_2\{P_2(O_2Pb)_3\}Cl_4].5H_2O$, and a basic salt. G. Quesneville prepared **platinous bisphosphaminodiamminechloride,** $[Pt(NH_3)_2\{P(NH_2)_3\}_2]Cl_2$, as a double salt with ammonium chloride; and **platinous chlorophosphaminediamminochloride,** $[Pt(NH_3)_2\{P(NH_2)_3\}Cl]Cl$, as a double salt associated with ammonium chloride; and it also occurs as a *heptahydrate.* G. Quesneville reported **platinous hydroxychlorophosphotrianilide,** $[Pt\{P(C_6H_6N)_3\}(OH)Cl]$, **platinous hydroxychlorophosphotritoluidide,** $[Pt\{(C_7H_8N)_3\}(OH)Cl$; **anilinium phosphotrianilidetrichloroplatinite,** $[Pt\{P(C_6H_6N)_3\}Cl_3]H(C_6H_5NH_2)$; and **toluidinium phosphotritoluididetrichloroplatinite,** $[Pt\{P(C_7H_8N)_3\}Cl_3]H(C_7H_7NH_2)$.

A. Cahours and H. Gal prepared **platinous quatertriethylarsinechloride,** $[Pt\{As(C_2H_5)_3\}_4]Cl_2$; **platinous trans-dichlorobistriethylarsine,** $[Pt\{As(C_2H_5)_3\}_2Cl_2]$; and **platinous cis-dichlorobistriethylamine.** K. A. Jensen measured the dipole moments of *cis-* and *trans-*compounds with the phosphines, arsines, and stibines; and he prepared **platinous dichlorobistributylarsine,** $[Pt\{(C_4H_9)_3As\}_2Cl_2]$. R. Bunsen prepared **platinous dichloroxycacodyl,** $[Pt\{As(CH_3)_4O\}Cl_2]$, and the cacodyl compounds were studied by K. A. Jensen and E. Frederiksen. A. W. Hofmann, and K. A. Jensen prepared **platinous dichlorobistriethylstibine,** $[Pt\{Sb(C_2H_5)_3\}_2Cl_2]$; and K. A. Jensen, **platinous dichlorobistributylstibine,** $[Pt\{(C_4H_9)_3Sb\}_2Cl_3]$; and **platinous dichlorobistriphenylstibine,** $[Pt\{(C_6H_5)_3Sb\}_2Cl_2]$, and he measured their dipole moments.

Chloroplatinites.—L. N. Vauquelin,[10] and G. Magnus prepared **ammonium chloroplatinite,** $(NH_4)_2PtCl_4$, by evaporating a mixed soln. of platinous chloride and ammonium chloride in hydrochloric acid, and drying the crystals at 100°. M. Peyrone saturated a soln. of platinous chloride in hydrochloric acid with ammonium carbonate, evaporated the soln. to dryness on a water-bath, washed the reddish residue repeatedly with alcohol to remove the ammonium chloride, exposed the product in air so as to remove all traces of alcohol, dissolved the product in boiling water, and filtered the hot liquid. When the liquid is allowed to cool slowly, prismatic crystals are deposited. L. F. Nilson obtained the salt by adding ammonium chloride to the mother-liquors obtained in the preparation of very soluble chloroplatinites. J. Thomsen added hydrochloroplatinic acid to a hot soln. of potassium chloroplatinite, added ammonium chloride to the filtered liquid, and evaporated the liquid for crystallization. P. Berthier added ammonium

sulphite to a soln. of hydrochloroplatinic acid, and obtained a yellow precipitate which dissolved when the mixture was warmed; the liquid then decolorizes, and on evaporation deposits crystals of the chloroplatinite. C. E. Claus, P. Schottländer, and K. Birnbaum reduced a warm soln. of hydrochloroplatinic acid or ammonium chloroplatinate with sulphur dioxide, added ammonium chloride, and evaporated the liquid for crystallization. J. Thomsen reduced the soln. with cuprous oxide or chloride; and E. Biilmann and A. C. Andersen, with ammonium oxalate. J. Thomsen treated copper ammonium chloroplatinite with hydrogen sulphide to precipitate the copper, acidified the filtrate with hydrochloric acid, and evaporated for crystallization. The purple-red or garnet-red, four-sided prisms or plates were found by H. Töpsöe to belong to the cubic system. H. Schröder gave 2·936 for the sp. gr., and H. Töpsöe, 145·6 for the mol. vol. L. F. Nilson observed that the salt is stable in air. J. Thomsen found the heat of formation (Pt, Cl_2, $2NH_4Cl$)=45·17 Cals., and (Pt, Cl_2, $2NH_4Cl$, Aq.)=41·38 Cals. L. F. Nilson found the salt to be sparingly soluble in cold water, and freely soluble in hot water; L. Tschugaeff and W. Chlopin found that in the presence of ammonia and ammonium carbonate, hydrogen peroxide acts on ammonium chloroplatinite to form the hydroxychloroplatinate. H. D. K. Drew and co-workers studied the action of ammonia—*vide* the potassium salt. M. Peyrone said that the salt is insoluble in alcohol and that the presence of alcohol produces some peculiar change in the salt which interferes with its crystallization. L. N. Vauquelin observed that the cold, aq. soln. gives no precipitate with soda-lye, but with hot soln., a black precipitate is produced and ammonia is evolved. L. A. Tschugaeff, and M. Vèzes described the preparation of the chloroplatinites.

G. Magnus prepared **potassium chloroplatinite,** K_2PtCl_4, by transforming hydrochloroplatinic acid into hydrochloroplatinous acid by heat, and mixing a soln. of the product with potassium chloride. M. C. Lea, and H. Wolffram added that the reduction of the hydrochloroplatinic acid is incomplete, even at 250° to 300°. R. Böttger reduced a soln. of potassium chloroplatinate with hydrogen sulphide, by passing the gas until half the platinum was precipitated, and evaporating the filtered soln. P. Klason, C. W. Blomstrand, M. Gröger, L. Wöhler and W. Frey, H. Wolffram, M. C. Lea, N. S. Kurnakoff, L. Pigeon, C. Rudelius, and J. Petren reduced the warm soln. of potassium chloroplatinate, or hydrochloroplatinic acid with sulphur dioxide or sulphurous acid; M. C. Lea, and M. Gröger, with potassium hydrosulphite; M. Gröger, with potassium hyposulphite; M. C. Lea, potassium hypophosphite; M. Vèzes, E. V. Zappi, H. Wolffram, and P. Klason, potassium oxalate; and J. Thomsen, E. Koefoed, H. Wolffram, M. Gröger, and M. C. Lea, cuprous chloride. L. F. Nilson obtained the salt by adding potassium chloride to the mother-liquors obtained in preparing more soluble chloroplatinites.

The salt is variously described as furnishing brownish-red, or ruby-red, four-sided prisms, and A. E. Nordenskjöld found the crystals to be tetragonal bipyramids with $a:c=1:0·4161$. R. G. Dickenson found that the X-radiograms corresponded with a tetragonal lattice having a=6·99 A., and c=4·13 A. W. Jander, A. G. Boldyrew and W. W. D. Dobrowolsky, and L. Pauling and M. L. Huggins made some observations on the lattice structure. A. Streng also described the crystals and observed a feeble dichroism. F. W. Clarke gave 3·291 to 3·306 for the sp. gr.; and R. G. Dickenson calculated 3·39 from the X-radiograms. R. Klement gave 3·382 for the sp. gr. at 25°/4°, and 122·7 for the mol. vol. I. Traube gave for the sp. gr., and mol. soln. vol.:

K_2PtCl_4 . . .	2·791	4·349	6·958	8·973 per cent.
Sp. gr. . . .	1·01962	1·03221	1·05395	1·07120
Mol. soln. vol. .	103·5	101·2	100·0	100·2

L. F. Nilson observed that the salt is stable in air, and at 100°, or confined over sulphuric acid, it slowly loses about 1 per cent. of water which cannot be removed from the crystals by pressure between bibulous paper. The ordinary salt decrepi-

tates when heated, but not so if it has been previously dried. J. Petersen found the lowering of the f.p., and the calculated mol. wt.:

K_2PtCl_6 . .	1·150	2·532	3·147	7·715 per cent.
Lowering f.p. . .	0·145°	0·290°	0·355°	0·900°
Mol. wt. . .	357	395	399	386—Theory, 415

The calculated values for the J. H. van Hoff's coeff.—**1.** 15, 10—range from 2·32 to 2·96. J. Thomsen found the heat of formation (Pt, Cl_2, 2KCl)=45·17 Cals.; (Pt, Cl_2, 2KCl, Aq.)=41·8 Cals.; and the heat of soln., −12·22 Cals. J. Lifschitz and E. Rosenbohm studied the optical properties; D. P. Mellor and F. M. Quodling, the birefringence; S. Aoyama and co-workers, the X-ray spectrum; and R. Samuel and co-workers, the absorption spectrum. A. Werner and A. Miolati measured the mol. conductivity of soln. with a mol of the salt in *v* litres, at 25°, and observed:

v	250	500	1000	2000
μ	251·6	260·4	267·6	279·3

N. Demassieux and J. Heyrovsky studied the dissociation of the salt in soln.; E. R. Smith, the potential of the chloroplatinate-chloroplatinite electrode; W. Schneider, the piezoelectric effect. E. Feytis gave for the magnetic susceptibility, $-0·356\times10^{-6}$ mass unit. E. Rosenbohm studied the subject. G. Magnus said that the salt readily dissolves in water, forming a reddish-yellow soln.; and W. Crookes observed that 100 parts of water dissolve 0·926 part of the salt at 16°, and 5·263 parts with boiling soln. According to J. Lang, a soln. of the salt is coloured brownish-black by hydrogen sulphide, and with hot soln., a black precipitate is formed; ammonium sulphide gives a black precipitate. W. Peters observed that no ammonia is absorbed by the dry salt; and J. Lang, that with aq. ammonia, green platinous tetramminochloroplatinite is formed; ammonium carbonate also decolorizes the hot soln. H. D. K. Drew and co-workers symbolized the reaction with ammonia: $K_2PtCl_4 \rightarrow K_2Pt(NH_3Cl)Cl_3 \rightarrow Pt(NH_3Cl)Cl$; and by $K_2PtCl_4 \rightarrow K_2Pt(NH_3Cl)_2Cl_2 \rightarrow Pt(NH_3Cl)_2$. A. Sieverts studied the action of sodium hypophosphite on dil. soln. of potassium chloroplatinite resulting in the formation of colloidal soln. of platinum. M. Vèzes observed that potassium nitrite forms a chloronitrite. E. Biilmann and A. C. Andersen found that allyl alcohol makes the red soln. pale yellow, and $K[Pt(C_3H_5OH)Cl_3]$ is formed. K. Birnbaum showed that complex salts are formed with ethylene, propylene, and amylene; E. Koeofed, that dimethylamine forms $[Pt\{(CH_3)_2NH\}_2Cl_2]$, and diethylamine gives a precipitate mainly of platinum black; and N. S. Kurnakoff, that acetamide, with a warm soln., forms blue and violet colours, and propionamide, butylamide, capronamide, succinimide, and phthalimide give blue colours, whilst thiourea furnishes complex salts, and guanidine or guanidine carbonate, in boiling soln., gives a greenish-black precipitate. J. Lang found that a soln. of potassium hydroxide has no reaction on a hot or cold soln. of the salt, but potassium and sodium carbonates produce a black precipitate which settles very slowly. H. Schwarz studied some reactions of the salt; and A. Grünberg, the nature of the *trans*-effect with the $PtCl''_4$-ions.

L. F. Nilson prepared **rubidium chloroplatinite,** Rb_2PtCl_4, by adding hydrochloroplatinous acid to a soln. of rubidium chloride, drying the salt on a water-bath, extracting the salt with water, drying the salt between bibulous paper and then over sulphuric acid or at 100°. R. Böttger passed hydrogen sulphide through a soln. of rubidium chloroplatinate until half the platinum is precipitated, and evaporated the filtrate. The red, or brownish-red, four-sided prisms are stable in air. L. F. Nilson said that the salt is sparingly soluble in cold water and freely soluble in hot water; and W. Crookes added that 100 parts of water dissolve 0·135 part of salt at 15·5°, and 0·637 part in boiling water. L. F. Nilson also prepared **cæsium chloroplatinite,** Cs_2PtCl_4, by adding cæsium sulphate to a soln. of barium chloroplatinite. L. Wöhler and F. Martin reduced a soln. of hydrochloro-

platinic acid to hydrochloroplatinous acid, by means of sulphur dioxide, then added a soln. of cæsium chloride, and separated the crystals on a suction-filter; R. Böttger employed hydrogen sulphide as reducing agent—*vide supra*. The crystals were also examined by E. H. Ducloux. The salt appears in brownish-red or flesh-red, four-sided prisms, which R. Godeffroy said can be melted without decomposition. L. F. Nilson observed that the salt is sparingly soluble in cold water and freely soluble in hot water; and W. Crookes added that 100 parts of water dissolve 0·0764 part of the salt at 15·5°, and 0·383 part in boiling water. According to R. Godeffroy, the solubility, S parts of salt per 100 parts of water, was found to be :

	20°	40°	60°	80°	100°
S	3·4	6·73	8·68	10·92	12·10

L. F. Nilson prepared **lithium chloroplatinite,** $Li_2PtCl_3.6H_2O$, by saturating a soln. of hydrochloroplatinous acid with lithium carbonate, evaporating the soln. spontaneously and drying the crystals at 100°. The dark green, four-sided prisms resemble the crystals of potassium permanganate. They deliquesce in air; and are freely soluble in water. G. Magnus prepared **sodium chloroplatinite,** Na_2PtCl_4, as the *tetrahydrate*, by adding sodium chloride to hydrochloroplatinous acid—*vide supra*, the potassium salt; J. Lang, by treating a soln. of platinous chloride in hydrochloric acid with sodium carbonate, evaporating the soln. to dryness, extracting the residue with alcohol, and evaporating at a gentle heat; and L. F. Nilson, by saturating a soln. of hydrochloroplatinous acid with sodium carbonate, evaporating the soln. to dryness, dissolving the residue in water and crystallizing—the first crop of crystals is the chloroplatinate. The red, four-sided prisms were found by L. F. Nilson to deliquesce a little in moist air, and to effloresce in dry air. The salt melts at 100°, and slowly gives off water. L. Wöhler and P. Balz found that the salt is stable above 800°. J. Thomsen gave for the heat of formation ($Pt, Cl_2, 2NaCl$)=41·38 Cals. W. Peters observed that the salt becomes anhydrous at 150°, forming a dark brown mass. L. F. Nilson said that the salt is soluble in water; and G. Magnus, that it is soluble in alcohol. W. Peters observed that the anhydrous salt slowly absorbs ammonia, forming **sodium tetramminochloroplatinite,** $Na_2PtCl_4.4NH_3$, and that in vacuo, the tetrammine passes into **sodium triamminochloroplatinite,** $Na_2PtCl_4.3NH_3$.

L. F. Nilson obtained **copper chloroplatinite,** $CuPtCl_4.6H_2O$, by saturating hydrochloroplatinous acid with copper carbonate, evaporating the soln. to dryness, extracting with water, and crystallizing the aq. soln. The olive-brown crystals are stable in air; they melt at 100° and give off 5 mols. of water. The salt is freely soluble in water. G. B. Buckton, and C. W. Blomstrand observed that with aq. ammonia there is formed **copper tetramminochloroplatinite,** $[Cu(NH_3)_4]PtCl_4$, in olive-green crystals which are decomposed by boiling water, forming $[Pt(NH_3)_2Cl_2]Cl_2$. The colour of the salt was discussed by N. S. Kurnakoff. E. Millon and A. Commaille prepared **platinous tetramminochlorocuprate,** $[Pt(NH_3)_4]CuCl_4$, by adding a conc. soln. of hydrochloroplatinic acid to an ammoniacal soln. of cuprous chloride; and J. Thomsen, by dissolving cuprous chloride in hydrochloroplatinic acid, and precipitating with aq. ammonia, or by mixing ammonium chloroplatinite with an ammoniacal soln. of a cupric salt. The salt furnishes violet or grey, four-sided prisms which are stable when dry at 150°, but at a higher temp. decompose leaving cuprous chloride and platinum behind. The salt is almost insoluble in water, but it is partially decomposed by a protracted washing. It is freely soluble in warm hydrochloric acid, and when ammonia is added to this soln. the original compound is re-precipitated. Part of the copper is precipitated as cupric sulphide when hydrogen sulphide is passed into water containing the salt in suspension, and afterwards the platinum is all precipitated as sulphide. Conc. sulphuric acid decomposes the salt energetically. Aq. ammonia forms a blue soln. and brown precipitate, $PtO(NH_3)_2$, and the blue

soln. is decolorized when boiled, forming a black precipitate ; the filtrate contains ammonium chloride and $[Pt(NH_4)_4]Cl_2$. When the soln. in dil. hydrochloric acid is treated with ammonium carbonate nearly all the copper is precipitated as basic chloride. The salt is insoluble in alcohol. The salt gives off ammonia when treated with potassium hydroxide, and when the mixture is boiled, a brown substance is formed which, when washed, dried, and heated, explodes. N. S. Kurnakoff, and S. G. Hedin noted the formation of **copper quaterpyridinochloroplatinite,** $CuCl_2.2PtCl_2(C_5H_5N)_4.12H_2O$; and **platinous quaterpyridinochlorocuprate,** $PtCl_2.2CuCl_2(C_5H_5N)_4$; and N. S. Kurnakoff, **copper quaterethylenediaminochloroplatinite,** Cu $en_4.2PtCl_2.9H_2O$.

A. Commaille reported *silver trichloroplatinite,* $AgPtCl_3$, to be formed by adding sufficient silver nitrate to a warm soln. of hydrochloroplatinic acid, and drying the precipitate at 120°. The yellow product becomes grey when exposed to light. When treated with ammonia it gives silver chloride, and some hydrochloroplatinic acid is formed. A boiling ammoniacal soln. of alcohol precipitates platinum black. S. M. Jörgensen considered that this product is a mixture. W. Peters, and J. Lang prepared **silver chloroplatinite,** Ag_2PtCl_4, by the action of silver nitrate on potassium chloroplatinite. The pale red precipitate blackens in light. It is insoluble in cold and boiling water, but it becomes dark yellow when boiled with water. Hydrochloric acid slowly, rapidly when warm, extracts all the platinous chloride. Aq. ammonia extracts the silver chloride ; and gaseous ammonia forms an approximation to **silver hexamminochloroplatinite,** $Ag_2PtCl_4.(6+1\frac{1}{2})NH_3$, and this product in vacuo forms approximately **silver triamminochloroplatinite,** $Ag_2PtCl_4.(3+1\frac{1}{2})NH_3$. J. Thomsen mixed ammoniacal soln. of silver chloride with ammonium chloroplatinite and obtained rose-red needles of **silver tetramminochloroplatinite,** $Ag_2PtCl_4.4NH_3$, which lose ammonia when dried, forming a green substance which when heated gives off ammonium chloride, leaving a residue of silver chloride and platinum. L. Tschugaeff and N. K. Pschenicyn studied the depolymerization of $[Ag(NH_3)]_2PtCl_4$. N. S. Kurnakoff obtained **silver ethylenediaminechloroplatinite,** $Ag\{C_2H_4(NH_2)_2\}PtCl_3$; and S. M. Jörgensen one with ethylene. From the observations of W. Peters it is probable that hydrochloroplatinous acid and auric chloride probably give a precipitate of gold instead of forming **gold chloroplatinite.**

L. F. Nilson reported that **calcium chloroplatinite,** $CaPtCl_4.8H_2O$, is not formed when impure hydrochloroplatinous acid is treated with calcium oxide, but if the purified acid is employed, and the soln. evaporated over sulphuric acid, thin, four-sided plates of the salt are formed. The salt is deliquescent in moist air ; it effloresces in dry air ; it melts at 100°, and slowly loses 5 mols. of water passing into the chloroplatinate and platinum. L. F. Nilson prepared **strontium chloroplatinite,** $SrPtCl_4.6H_2O$, by mixing purified hydrochloroplatinous acid with the theoretical proportion of strontium chloride, evaporating to dryness, extracting with water, and evaporating the soln. over sulphuric acid. The thin, four-sided plates effloresce over sulphuric acid ; they melt at 100° with the evolution of two-thirds the water of hydration ; they deliquesce in moist air ; and they are freely soluble in water. L. F. Nilson prepared **barium chloroplatinite,** $BaPtCl_4.3H_2O$, by saturating hydrochloroplatinous acid with barium carbonate, and crystallizing the soln. J. Lang observed that with the spontaneous evaporation of the soln., barium chloride is first precipitated. The four-sided prisms are coloured a darker red than the potassium salt. The salt loses 2 mols. of water at 100°, without decomposition, and the last mol. of water is expelled at 150°. The salt is readily dissolved by water, and with ammonia it forms green platinous tetramminochloroplatinite.

L. F. Nilson prepared **beryllium chloroplatinite,** $BePtCl_4.5H_2O$, by saturating hydrochloroplatinous acid with beryllium carbonate, evaporating the soln. to dryness on a water-bath, extracting with water, precipitating the hydrochloroplatinic acid as ammonium chloroplatinate, and concentrating the filtrate over sulphuric acid.

The ruby-red, rhombohedral crystals do not change in dry air, but they deliquesce in moist air ; at 100°, water and hydrogen chloride are evolved. The salt dissolves in water in all proportions. L. F. Nilson prepared **magnesium chloroplatinite,** $MgPtCl_4.6H_2O$, by a similar process. The four-sided or six-sided plates are fairly stable in air ; they lose hygroscopic moisture at 100° : and are very soluble in water.

F. L. Hünefeld partially precipitated an aqua regia soln. of platinum with zinc until the soln. had acquired a pale yellow colour, and evaporated the filtrate. The first crop of crystals of **zinc chloroplatinite,** $ZnPtCl_4.6H_2O$, is followed by a crop of crystals of the chloroplatinate. If the zinc acts for a short time only, the chloroplatinate is the main product, but if the action be continued until a yellow powder is precipitated with the platinum, and the liquid be then boiled and filtered, the chief product is the chloroplatinite. L. F. Nilson obtained the salt by double decomposition of barium chloroplatinite and zinc sulphate. The pale yellow crystals become dark orange when heated, and then yellowish-brown. The hexahydrate gives off all the combined water at 100°, without melting. At a high temp. the salt is resolved into zinc chloride, platinum and chlorine with a " transient jumping motion." The salt is sparingly soluble in cold water, more easily soluble in boiling water, and the original salt separates out on cooling, or on the addition of alcohol. The aq. soln. gives a brown precipitate with ammonium sulphide ; and the salt is but slightly attacked by sulphuric acid. The aq. soln. gives a yellow precipitate with a soln. of cuprous chloride in hydrochloric acid ; and a dingy flesh-coloured precipitate with silver nitrate. G. B. Buckton obtained **platinous tetrammino-chlorozincate,** $[Pt(NH_3)_4]ZnCl_4$, from a conc. soln. of platinous tetramminochloride and zinc chloride. The colourless plates are soluble in water. J. Thomsen, and N. S. Kurnakoff prepared **zinc tetramminochloroplatinite,** $[Zn(NH_3)_4]PtCl_4$, by adding ammonium chloroplatinite to an ammoniacal soln. of zinc chloride. The reddish needles are slightly soluble in water, and freely soluble in hydrochloric acid, from which soln. the salt is precipitated unchanged on adding aq. ammonia. L. Tschugaeff and N. K. Pschenicyn studied the depolymerization of this salt. S. G. Hedin obtained a complex salt with pyridine.

L. F. Nilson prepared **cadmium chloroplatinite,** $CdPtCl_4$, in soln., but not in the solid state from soln. of cadmium sulphate and hydrochloroplatinous acid, or of barium chloroplatinite. The soln. deposits cadmium chloride when evaporated. J. Thomsen prepared brick-red **cadmium tetramminochloroplatinite,** $[Cd(NH_3)_4]PtCl_4$, as in the case of the corresponding zinc compound.

L. F. Nilson did not prepare **mercury chloroplatinite** by the evaporation of a soln. of mercuric chloride in hydrochloroplatinous acid, since the mercuric chloride crystallizes out unchanged. Mercurous nitrate gives a dark brown precipitate when added to a soln. of potassium chloroplatinite, but the precipitate soon becomes black. G. B. Buckton prepared platinous tetramminochloromercurate, $[Pt(NH_3)_4]HgCl_4$, by treating platinous tetramminochloride with mercuric chloride, and drying the crystalline precipitate at 120°. The salt crystallizes during the cooling of a boiling soln. The salt is insoluble in hydrochloric acid. C. Rudelius prepared a complex with propyl sulphide ; and J. Petren, one with ethyl selenide. J. J. Berzelius reported a **mercurosic oxychloroplatinite,** $2HgO.2HgCl.PtCl_2.5H_2O$, to be formed by the action of mercurous nitrate on hydrochloroplatinic acid ; and A. Commaille also obtained the same product. The brown precipitate when heated furnishes a sublimate of mercurous chloride, and a residue of platinous oxide—the sublimate also contains a little mercuric oxide, and chloride. Aq. ammonia quickly blackens the compound, and potash-lye acts more rapidly. Boiling hydrochloric acid forms platinum black ; and boiling nitric acid dissolves it slowly and completely.

L. F. Nilson obtained **aluminium chloroplatinite,** $AlPtCl_5$, from a soln. of equimolar proportions of aluminium chloride and hydrochloroplatinous acid ; and from the filtrate after mixing soln. of aluminium sulphate and barium chloro-

platinite. The four-sided, prismatic crystals deliquesce in air, they melt at 100° slowly giving off 9½ mols. of water. L. F. Nilson could not prepare **indium chloroplatinite.** L. F. Nilson prepared **thallous chloroplatinite,** Tl_2PtCl_4, by mixing warm soln. of thallous sulphate and an alkali or ammonium chloroplatinite. The salt is recrystallized from boiling water, and dried at 100°. The salt is sparingly soluble in boiling water. S. Meyer found the magnetic susceptibility at 20° to be $-0{\cdot}205\times10^{-6}$ mass unit.

L. F. Nilson prepared **cerous chloroplatinite,** $CeCl_3.2PtCl_2.10{\cdot}5H_2O$, in thin, four-sided prisms which lose 15 mols. of water at 100°; **lanthanum chloroplatinite,** $2LaCl_3.3PtCl_2.18H_2O$, in thin, four-sided prisms, and also $2LaCl_3.3PtCl_2.27H_2O$, in prisms which lose 16 mols. of water at 100°; **didymium chloroplatinite,** $2DiCl_3.4PtCl_2.2H_2O$, in prisms or plates which are deliquescent in air, and $2DiCl_3.3PtCl_2.18H_2O$, in prismatic crystals; **erbium chloroplatinite,** $2ErCl_3.2PtCl_2.27H_2O$, in dark red prisms, which lose 17 mols. of water at 100°, and $2ErCl_3.3PtCl_2.24H_2O$, in long, four-sided prisms, which lose 11 mols. of water at 100°; **yttrium chloroplatinite,** $2YCl_3.3PtCl_2.24H_2O$, in dark red, four-sided prisms, which melt at 100°, losing 10 mols. of water; **thorium chloroplatinite,** $2ThCl_4.3PtCl_2.24H_2O$, in rhombohedral crystals, which lose one-fourth of their water of hydration at 100° without melting; and **zirconyl chloroplatinite,** $ZrOCl_2.PtCl_2.8H_2O$, in quadratic prisms.

R. J. Kane obtained greenish-brown, deliquescent crystals of **stannous chloroplatinite,** which are decomposed by water, and also a chloroplatinite with more tin. This salt forms a red soln. in water, and the salt is hydrolyzed. G. B. Buckton treated platinous tetramminochloride with an acid soln. of stannous chloride and obtained **stannous tetramminochloroplatinite,** $[Pt(NH_3)_4]SnCl_4$, and likewise **stannic tetramminochloroplatinite,** $[Pt(NH_3)_4]SnCl_6$. C. Rudelius obtained a complex with propyl sulphide. J. Lang treated a soln. of lead nitrate or acetate with potassium chloroplatinite and obtained **lead chloroplatinite,** $PbPtCl_4$, as a pale red, amorphous precipitate, which is decomposed slowly by boiling water. G. B. Buckton mixed soln. of platinous chloroplatinite and lead acetate, and obtained four-sided plates of **lead tetramminochloroplatinite,** $[Pb(NH_3)_4]PtCl_4$, which are not decomposed at 170°; and are insoluble in hydrochloric acid, and in alcohol.

L. F. Nilson obtained **chromic chloroplatinite,** $2CrCl_3.3PtCl_2.18H_2O$, by evaporating in vacuo the filtrate from a mixture of soln. of equimolar parts of violet chromic sulphate and barium chloroplatinite. The red deliquescent prisms lose water and hydrogen chloride at 100°. S. M. Jörgensen prepared **chromic hydroxychlorohexamminochloroplatinite,** $[Cr_2(NH_3)_6(OH)_2Cl_3]_2PtCl_4$. L. F. Nilson also obtained **manganese chloroplatinite,** $MnPtCl_4.6H_2O$, from barium chloroplatinite and manganese sulphate. The crystals lose 4 mols. of water at 100°. The crystals were examined by H. Töpsöe and H. Christiansen.

L. F. Nilson obtained **ferrous chloroplatinite,** $FePtCl_4.7H_2O$, from the filtrate from a mixture of soln. of ferrous sulphate and barium chloroplatinite. The deliquescent, dark red prisms lose 5 mols. of water at 100°. According to G. B. Buckton, ferrous salts do not unite with platinous tetramminochloride, and ferric chloride transforms it into platinic dichlorotetramminochloride.

L. F. Nilson obtained **cobalt chloroplatinite,** $CoPtCl_4.6H_2O$, by evaporating, over sulphuric acid, a soln. of hydrochloroplatinous acid saturated with cobalt chloride. Crystals of cobalt chloroplatinate are first deposited, and then crystals of the chloroplatinite in four-sided or six-sided plates which are deliquescent in moist air, and efflorescent in dry air. The salt loses 5 mols. of water at 100°. N. S. Kurnakoff prepared **cobalt hexamminochloroplatinite,** $[Co(NH_3)_6]PtCl_4$, in yellowish-red plates; and also **platinous tetramminochlorocobaltite,** $[Pt(NH_3)_4]CoCl_4$, from a mixture of soln. of platinous tetramminochloride and cobalt chloride. The complexes **cobaltous quaterpyridinochloroplatinite,** $Co\,py_4PtCl_4$, and **cobaltous trisethylenediaminochloroplatinite,** $Co\,en_2PtCl_4$, were

also obtained. A. Werner, and S. M. Jörgensen prepared complex chloroacetates ; S. M. Jörgensen, complex chloroxalates ; and A. Werner and H. Müller, complex chlorothiocyanates. A. Werner and A. Klein prepared **cobaltic dichlorotetramminochloroplatinite,** $[Co(NH_3)_4Cl_2]_2PtCl_4$, as a green, unstable powder, by the action of potassium chloroplatinite on cobaltic bisdichlorotetramminosulphate. N. S. Kurnakoff studied the salt. S. M. Jörgensen prepared **cobaltic dinitritotetramminochloroplatinite,** $[Co(NO_2)_2(NH_3)_4]_2PtCl_4$; and **cobaltic trisethylenediaminechloroplatinite,** $[Co\,en_3]_2(PtCl_4)_3$; **cobaltic chlorobisethylenediamineamminochloroplatinite,** $[Co(NH_3)\,en_2Cl]PtCl_4$; A. Werner and R. Feenstra, **cobaltic dichloroquaterpyridinechloroplatinite,** $[Co\,py_4Cl_2]PtCl_4$; A. Werner and A. Fröhlich, **cobaltic dichlorobispropylenediaminechloroplatinite,** $[Co\,pn_2Cl_2]_2PtCl_4$; A. Werner and E. Kindscher, **cobaltic dioloctamminochloroplatinite,** $[Co_2(OH)_2(NH_3)_8]PtCl_4$.

L. F. Nilson prepared **nickel chloroplatinite,** $NiPtCl_4.6H_2O$, by saturating hydrochloroplatinous acid with nickel carbonate, evaporating the soln. to dryness, extracting the product with water, precipitating the hydrochloroplatinic acid as ammonium chloroplatinate, and concentrating the filtrate over sulphuric acid. The dark brown plates are deliquescent in moist air, efflorescent in dry air ; and they lose 3 mols. of water at 100°. J. Thomsen, and N. S. Kurnakoff prepared **nickel tetramminochloroplatinite,** $[Ni(NH_3)_4]PtCl_4$; and N. S. Kurnakoff, **nickel hexamminochloroplatinite,** $[Ni(NH_3)_6]PtCl_4$; and he also obtained complexes with ethylenediamine. H. D. K. Drew and co-workers prepared from the tetrammine and aq. soln. of potassium chloropalladite or chloroplatinite, **palladous tetramminochloroplatinite,** $[Pd(NH_3)_4]PtCl_4$, in pink needles ; and **palladous bispyridinodiamminochloroplatinite,** $[Pd(NH_3)_2(C_5H_5N)_2]PtCl_4$. Complex **platinous chloroplatinites** have been discussed above.

Hydroxychloroplatinites.— R. J. Kane [11] prepared **platinous trioxydichloride,** $PtCl_2.3PtO$, by boiling a soln. of platinic chloride with conc. sulphuric acid almost to dryness ; and washing the black product with water. At a red-heat, chlorine and water are evolved, and platinum remains. Hydrochloric acid dissolves it as hydrochloroplatinous acid ; ammonia transforms it into an explosive compound ; and it is soluble in potash-lye. According to A. Miolati and U. Pendini, the aq. soln. contains **hydroxytrichloroplatinous acid,** $H_2[Pt(OH)Cl_3]$. The reddish-brown aq. soln. has an acidic reaction, and it furnishes precipitates of the silver and lead salts when treated with, respectively, silver and lead acetates. They prepared **potassium hydrochloroplatinite,** $K_2Pt(OH)Cl_3$, in acicular crystals, by neutralizing a soln. of the acid with potassium hydroxide, and evaporating over sulphuric acid. A brown precipitate of **silver hydroxychloroplatinite,** $Ag_2Pt(OH)Cl_3$, is produced by adding silver acetate to a conc. soln. of hydroxychloroplatinous acid. By evaporating a soln. of hydrochloroplatinous acid at 50° to 60°, a soln. was obtained which, with silver nitrate, gave a precipitate of **silver dihydroxychloroplatinite,** $Ag_2Pt(OH)_2Cl_2$. By saturating a soln. of hydroxychloroplatinous acid with lead acetate, a dark brown precipitate of **lead hydroxychloroplatinite,** $PbPt(OH)Cl_3$, was formed.

G. Gore [12] said that when silver fluoride is fused in an atm. of chlorine in a platinum crucible, **silver fluochloroplatinate,** $4Ag(Cl.,F).PtCl_4$, is formed. J. Petren reported **platinous chlorobromobisethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2ClBr]$, and **platinous chlorobromoethylsulphineethylselenine,** $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}ClBr]$.

P. C. Ray and co-workers [13] claimed to have prepared complexes containing **platinum hemipentachloride,** Pt_2Cl_5—*e.g.* $Pt_2Cl_5.3(CH)_2S_2$.

F. Martin,[14] and L. Wöhler and F. Martin heated platinous chloride in an atm. of chlorine at 390° to 400°, and obtained what was considered to be **platinum trichloride,** or **platinosic chloride,** $PtCl_3$, and they also obtained it by heating powdered platinic chloride for 10 hrs. at 390° in dry chlorine freed from hydrogen chloride. L. Pigeon also obtained it by heating platinum in chlorine for 6 hrs. at 360°, and cooling the product rapidly in an atm. of chlorine. G. Magnus probably

obtained the same product by heating hydrochloroplatinic acid to 220° to 250°. L. Wöhler and F. Martin said that the powder is black with a greenish tinge unlike platinum di- or tetra-chloride. R. Klement gave 5·256 for the sp. gr. at 25°/4°, and 57·4 for the mol. vol. S. Streicher, and L. Wöhler and S. Streicher said the decomposition temp. is 435°, and that the heat of formation is $(2PtCl_2, Cl_2) = 26\cdot2$ Cals. The trichloride was found by F. Martin, and L. Wöhler and F. Martin, to be reduced by hydrogen in the cold; it is slightly soluble in cold water, and only after several days is enough dissolved to impart to the soln. a yellow colour; it immediately dissolves in boiling water to form a brownish-red soln. which reacts acid, and probably contains **hydroxytrichloroplatinosic acid,** H_2PtOCl_3, as a result of hydrolysis. This same acid is formed when an aq. soln. of hydrochloroplatinic acid is reduced with sulphur dioxide. The aq. soln. of platinum trichloride yields the original salt if evaporated in vacuo at 60° and then at 100°; the salt is almost insoluble in conc. hydrochloric acid at ordinary temp., but the warm acid forms a yellow soln. containing platinic and platinous chlorides; it readily dissolves in an aq. soln. of potassium iodide, forming a dark brown liquid; and alcohol reduces it to metal at the same time forming aldehyde. The free acid, **hydrochloroplatinosic acid,** H_2PtCl_5, could not be isolated, but on passing a little chlorine into hydrochloroplatinous acid, the presence of tervalent platinum can be recognized by precipitation as a green cæsium salt, but decomposition sets in rapidly. L. Tschugaeff and I. Tscherniaeff studied the action of liquid ammonia on platinum trichloride. E. Müller and R. Bennewitz titrated soln. of tervalent platinum salts electrometrically with soln. of stannous chloride.

S. M. Jörgensen obtained a complex salt, **platinosic pyridineamminotrichloride,** $Pt(NH_3)(C_5H_5N)Cl_3$, or $Pt_2(NH_3)_2(C_5H_5N)_2Cl_6$. There are a few complex salts containing both platinous and platinic chlorides. Thus, P. C. Ray and co-workers obtained **platinosic bispyridinetrichloride,** $PtCl_3(C_5H_5N)_2$; and **platinosic quaterpyridinotrichloride,** $PtCl_3(C_5H_5N)_4$; and they discussed the varying valency of platinum with respect to the mercaptanic radicle. E. Biilmann and A. Hoff prepared **platinic allylacetictrichloride** as a double salt with platinous tetrammine, $[(C_3H_5.CH_2.COOH)PtCl_3]_2[Pt(NH_3)_4]$; and similarly with **platinic allylmalonictrichloride,** $[\{C_3H_5.CH(COOH)_2\}PtCl_3]_2[Pt(NH_3)_4]$; and with **platinic vinylacetictrichloride,** P. Pfeiffer and H. Hoyer prepared a series: with allyl alcohol, $[Co\,en_2Cl_2][Pt(C_3H_5.OH)Cl_3]$; with allyl acetate, $[Co\,en_2Cl_2][Pt(CH_3.COOC_3H_5)Cl_3]$; with crotyl alcohol, $K[Pt(C_4H_7.OH)Cl_3]$; and in which $[Co\,en_2Cl_2]$, $[Co\,en_2(C_2O_4)]$, and $[Pt(NH_3)_4]$, respectively, take the place of potassium; with crotyl acetate, $[Co\,en_2Cl_2][Pt(C_6H_{10}O_2)Cl_3]$; and with crotonaldehyde, $[Co\,en_2Cl_2][Pt(C_3H_5.COH)Cl_3]$. A. Cossa, and S. G. Hedin prepared **platinous quaterpyridinechloroplatinate,** $[Pt(C_5H_5N)_4]PtCl_6$; A. Cossa, **platinic quaterethylaminechloroplatinite,** $[Pt(C_2H_5NH_2)_4Cl_2]PtCl_4$; J. E. Reynolds, G. Prätorius-Seidler, and N. S. Kurnakoff, **platinous quaterthiocarbamidechloroplatinite,** $[Pt\{CS(NH_2)_2\}_4]PtCl_6$; N. S. Kurnakoff, and H. Debus, **platinous quaterxanthogenamidechloroplatinate,** $[Pt(NH_2.CS.OC_2H_5)_4]PtCl_6$; L. Tschugaeff and J. Benewolensky, **platinous quatermethylsulphinechloroplatinate,** $[Pt\{(CH_3)_2S\}_4]PtCl_6$; and A. Cahours and H. Gal, **platinous quaterethylphosphinechloroplatinate,** $[Pt\{P(C_2H_5)_3\}_4]PtCl_6$. P. C. Ray and co-workers prepared **platinosic p-phenylenediaminotrichloride,** $PtCl_3.4C_6H_4(NH_2)_2$; **platinosic piperidinotrichloride,** $PtCl_3.2C_5H_{11}N$; **platinosic triethylenedisulphinotrichloride,** $PtCl_3.(C_2H_4)_2S_2$, or $Pt\{(C_2H_4)_3S_2\}Cl_2]Cl$; **platinosic benzylsulphinochloride,** $PtCl_3.2(CH_2.C_6H_5)_2S$, or $[Pt\{(CH_2.C_6H_5)_2S\}Cl_2]Cl$; and **platinosic trisethylenediaminetriethylenetrisulphinochloride,** $2PtCl_3.3C_2H_4(NH_2)_2.(C_2H_4)_3S_3$. There are also platinum quaterpyridinechloride, $Pt_2Cl_7.4C_5H_5N$; and platinum quaterdibenzylsulphinochloride, $Pt_2Cl_5.4(CH_2.C_6H_3)_2S$.

F. Martin, and L. Wöhler and F. Martin prepared **cæsium chloroplatinosate,** $2CsCl.PtCl_3$, or Cs_2PtCl_5, as a dark green, crystalline precipitate, by oxidizing cæsium chloroplatinite with chlorine water at 0°. In the case of potassium and rubidium salts, the chloroplatinates are formed. The salt is also formed by adding cæsium chloride to a well-cooled hydrochloric acid soln. of hydrated platinum sesquioxide, or by adding cæsium chloride to a cold soln. of platinum trichloride. The salt appears in dark green, cubic crystals. The salt readily decomposes into a mixture of cæsium chloroplatinite and chloroplatinate. In a warm aq. soln. the green colour quickly changes to yellow—characteristic of cæsium chloroplatinate. Sunlight accelerates the decomposition into the higher and lower chlorides. The salt also decomposes when heated, or when exposed to moist air.

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§ 22. Platinum Tetrachloride

L. Pigeon [1] observed that only a very small yield of anhydrous **platinic chloride,** or **platinum tetrachloride,** $PtCl_4$, is obtained by passing chlorine over heated, finely-divided platinum. At 360° di- and tetra-chlorides are formed, but a considerable proportion of the metal is not attacked. C. Nogareda found that the tetrachloride is formed between 600° and 850°. A. Gutbier and F. Heinrich added that the yield is not much better if platinum be heated with arsenic trichloride in a sealed tube. L. Pigeon recommended the following process:

Finely-divided, spongy platinum mixed with somewhat less than its own weight of selenium is placed in a stout glass tube one-third filled with arsenic trichloride, and a current of chlorine is passed in, the tube being gradually heated until the liquid boils. The platinum is rapidly and completely dissolved, and the tube is then sealed and heated at 250° for several hours. After cooling, the tube contains a pale yellow liquid, orange-yellow crystals, and also, if the selenium is in excess, colourless crystals. The crystals are separated and heated in vacuo at 110°. They then consist of platinum tetrachloride and selenium tetrachloride, and are heated at 360° in a current of chlorine, when selenium chloride sublimes and anhydrous platinum tetrachloride remains as a brown, very hygroscopic powder. At 440°, it is converted into the dichloride. If platinum selenide is used instead of a mixture of platinum and selenium, no action takes place even at 300°; if selenium is omitted altogether, the platinum is not completely attacked, but the action becomes complete if selenium is added.

H. Precht removed nitric acid by repeatedly evaporating the soln. of platinum in aqua regia alternately with hydrochloric acid and water. H. B. North obtained the tetrachloride by heating platinum wire with sulphuryl chloride in a sealed tube for many days at 150°. The anhydrous salt can be obtained by dehydrating the hydrated tetrachloride, or hydrochloroplatinic acid. Thus, L. Pigeon heated the

hydrate at 215° in vacuo in the presence of potassium hydroxide; A. Rosenheim and W. Löwenstamm heated hydrochloroplatinic acid in a current of dry chlorine at about 275°; and A. Gutbier and F. Heinrich, and L. von Müller added that this is by far the best mode of preparing the anhydrous salt, and L. Pigeon employed a modification of the process. L. Wöhler and F. Martin, and F. Martin passed a current of dry hydrogen chloride over dry hydrochloroplatinic acid at 275°, and W. Pullinger employed a similar process although A. Rosenheim and W. Löwenstamm, and A. Gutbier and F. Heinrich said that the product is a mixture of platinum di- and tetra-chlorides. L. Pigeon added the theoretical quantity of potassium iodide to a hot soln. of hydrochloroplatinic acid, and then passed chlorine over the washed and dried platinum tetraiodide heated by an oil-bath.

The salt has been obtained in soln. J. W. Mallet noticed that platinum black exposed to the atmosphere on a filter whilst in contact with conc. hydrochloric acid forms a yellow soln. containing platinic chloride. L. Opificius observed that when aqua regia acts on a mixture of platinum and ammonium chloroplatinate, and the temp. is gradually raised to boiling, whilst the soln. is evaporated, the reaction can be symbolized: $2Pt+(NH_4)_2PtCl_6+10HNO_3+6HCl=3PtCl_4+12H_2O+6NO_2+6NO$. The hydrated platinic chloride forms a clear soln. with alcohol showing that the ammonium salt has been all destroyed—*vide infra*, hydrochloroplatinic acid. According to J. Brown, commercial platinic chloride contains some iron salt; and, according to W. Gintl and B. Reinitzer, some auric chloride, and, according to A. F. Hollemann, some sulphuric acid. The subject was discussed by K. W. G. Kastner.

A number of definite hydrates have been reported. F. Reiff studied the tendency of the hydrates to form aquo-salts. According to L. Pigeon, the *monohydrate*, $PtCl_4.H_2O$, is formed when the higher hydrates are exposed over potassium hydroxide in vacuo at 100°. A. Gutbier and F. Heinrich said that this hydrate is formed when the anhydrous salt is exposed to air for a short time. S. M. Jörgensen observed that the monohydrate decomposes with the expulsion of the last mol. of water by heat. A. Miolati prepared the *tetrahydrate*, $PtCl_4.4H_2O$, by adding uranyl acetate to an alcoholic soln. of the pentahydrate, filtering off the precipitate and washing it with alcohol and ether, and drying it over conc. sulphuric acid in vacuo; M. Blondel, by drying the octohydrate over sulphuric acid in vacuo; R. Engel, by dissolving in a soln. of hydrochloroplatinic acid the quantity of hydrated platinic oxide necessary for neutralization; and evaporating the filtered liquid. R. Engel said that the crystals of the tetrahydrate are not deliquescent. S. A. Norton added 2 mols. of a soln. of silver nitrate to a soln. of a mol. of hydrochloroplatinic acid, and evaporated the filtered liquid over sulphuric acid. R. Engel represented the reaction: $H_2PtCl_6+2AgNO_3=2AgCl+2HNO_3+PtCl_4$. The analyses of the product by A. Gutbier and F. Heinrich, S. M. Jörgensen, L. Pigeon, and S. A. Norton agree with the analysis of the *pentahydrate*, $PtCl_4.5H_2O$. L. Pigeon evaporated a neutral soln. of platinic chloride in vacuo at not too high a temp., and obtained what he regarded as a *heptahydrate*, $PtCl_4.7H_2O$. C. H. D. Bödeker said that the ordinary hydrated platinic chloride is the *octohydrate*, $PtCl_4.8H_2O$, but, according to R. Engel, the partial analyses made by C. H. D. Bödeker may have applied to $H_2PtCl_6.6H_2O$ instead of to $PtCl_4.8H_2O$. M. Blondel obtained the octohydrate by dissolving at ordinary temp. a mol. of platinic oxide in 2 mols. of hydrochloric acid, allowing the soln. to crystallize, and drying the product in air at 15°; he also said that this hydrate is formed when an aq. soln. of the pentahydrate is allowed to crystallize. The report of W. W. Mather, H. Lawrow, and M. Protopoff that the ordinary salt is the *decahydrate*, $PtCl_4.10H_2O$, is considered by R. Engel to have been based on incomplete analyses of $H_2PtCl_6.6H_2O$, which contain very nearly the proportion of platinum required for $PtCl_4.10H_2O$. The assumed decahydrate was said to be obtained by evaporating an aq. soln. of platinic chloride, and cooling the liquid.

The anhydrous chloride furnishes reddish-brown or brown, tabular crystals,

which L. Wöhler and F. Martin said are very hygroscopic, and which W. Pullinger said are not hygroscopic. A. Rosenheim and W. Löwenstamm, and A. Gutbier and F. Heinrich observed that the crystals gradually absorb moisture from the air to form $PtCl_4.H_2O$, then $PtCl_4.5H_2O$, and finally $H_2PtOCl_4.4H_2O$. R. Engel observed that the crystals of the tetrahydrate are not deliquescent; and S. A. Norton that the pentahydrate furnishes red, monoclinic crystals which effloresce in ordinary, dry air, but, according to S. M. Jörgensen, they deliquesce a little in moist air. S. A. Norton observed no deliquescence in moist air. H. St. C. Deville and J. S. Stas said that the aq. soln. is yellow or orange-red. C. H. D. Bödeker gave 2·431 for the sp. gr. of the octohydrate at 15°; and R. Klement gave 4·303 for the sp. gr. at 25°/4°, and 78·3 for the mol. vol. H. Precht found the sp. gr. of aq. soln., containing p per cent. of platinic chloride, containing 2·24 parts of HCl for 100 parts of $PtCl_4$ to be :

p . .	1	5	10	15	20	25	30	40	50 per cent.
Sp. gr. .	1·009	1·046	1·097	1·153	1·214	1·285	1·362	1·546	1·785
Mol. vol. .	—	40·5	39·0	—	39·9	—	38·4	39·9	40·5

The mol. vols. are by I. Traube. G. T. Gerlach made some observations on the sp. gr. of soln.

According to L. Pigeon, the anhydrous chloride is stable up to 260°; but F. Martin, and L. Wöhler and F. Martin found that in an atm. of chlorine, the salt decomposes above 275°, and S. Streicher, and L. Wöhler and S. Streicher gave 370° for the temp. of formation and decomposition. L. Wöhler and F. Martin's observations on the range of stability of the platinum chlorides are summarized in Fig. 79. C. Nogareda studied the subject. A. Gutbier and F. Heinrich found

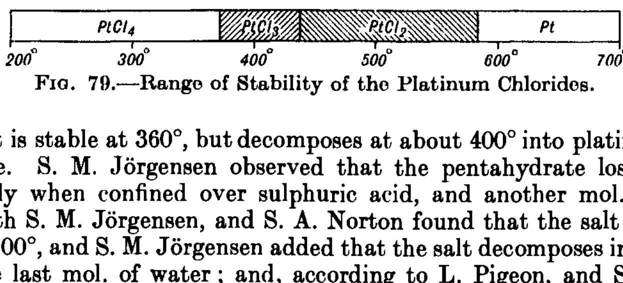


FIG. 79.—Range of Stability of the Platinum Chlorides.

that the salt is stable at 360°, but decomposes at about 400° into platinous chloride and chlorine. S. M. Jörgensen observed that the pentahydrate loses a mol. of water rapidly when confined over sulphuric acid, and another mol. is lost very slowly. Both S. M. Jörgensen, and S. A. Norton found that the salt loses 4 mols. of water at 100°, and S. M. Jörgensen added that the salt decomposes in the attempt to expel the last mol. of water; and, according to L. Pigeon, and S. A. Norton, platinous chloride is formed in the vicinity of 360°. C. Gordon stated that after 24 hrs.' heating of the hydrated salt to 150°, metallic platinum, and only a little platinous chloride, are formed. M. Blondel noticed that in vacuo over sulphuric acid, the octohydrate loses 4 mols. of water.

According to G. Oddo, the mol. wts. calculated from the f.p. of soln. of the anhydrous chloride in phosphoryl chloride for soln. of concentration 0·5410, 3·1874, and 3·7114, are, respectively, 171·23, 324·3, and 320·1. L. Pigeon gave for the heat of formation of the anhydrous tetrachloride, $(Pt, 2Cl_2)=59·4$ to 59·8 Cals.; and $(2PtCl_3, Cl_2)=23·55$ Cals.; for the heat of formation of the tetrahydrate from the anhydrous salt and liquid water, $(PtCl_4, 4H_2O)=21·32$ Cals.; and for the pentahydrate, 21·42 Cals. L. Pigeon also gave for the heat of soln. of the anhydrous salt, 19·58 Cals.; for that of the tetrahydrate, $-1·74$ Cals.; and for that of the pentahydrate, $-1·84$ Cals.

E. Doumer found the index of refraction of the soln. with respect to water to be 0·267. J. H. Gladstone gave 71·06 for the mol. refraction; 26·0 for the refraction equivalent; and 0·132 for the sp. refraction. Observations were also made by N. S. Kurnakoff. J. H. Gladstone and W. Hibbert found the mol. refraction of different soln. for the H_α-line and the D-line to be, respectively, 78·22 and 79·81 for 39·40 per cent. soln., 77·57 and 79·03 for 21·68 per cent. soln.; and 77·20 and 78·39 for 8·10 per cent. soln. A. Hantzsch, Y. Shibata and K. Harai, and R. Clark

and K. Meyer studied the absorption spectrum of aq. soln.; and A. Hébert and G. Reynaud, the absorption of X-rays. F. Kohlrausch observed that the hydrolysis of aq. soln. of platinic chloride proceeds in darkness, but more rapidly when exposed to sunlight. G. Foussereau observed that the conductivity of a soln. of concentration 1 : 1593 in darkness increases in 7 days from 0·038 to 0·051, and for a similar change in daylight, 5½ hrs. were needed, and in sunlight, 1 hour. F. Kohlrausch found that red, yellow, blue, and white light are increasingly efficient in increasing the speed of hydrolysis. A. F. Gehlen observed that when an ethereal soln. of platinic chloride is exposed to light, it becomes pale yellow and deposits platinum. The aq. soln. is not precipitated in the dark, either by an excess of sodium carbonate or by calcium carbonate, but on exposure to light a compound of platinic oxide with soda or lime is deposited. J. Fiedler observed that in light, platinum is reduced from a mixture of platinic chloride and oxalic acid; soln. of platinic chloride, or of potassium or sodium chloroplatinates are also reduced on exposure to light.

W. Hampe observed that an aq. soln. of platinic chloride is a good electrical conductor, and there is a deposition of platinum; a soln. in dry ether is electrically conducting; and a soln. in absolute alcohol conducts well, depositing platinum sponge. J. Wagner observed that the electrical conductivity of aq. soln. increases on standing so that a soln. of a mol of the pentahydrate in $v=200$ litres of water was at first $\mu=209{\cdot}5$, after standing an hour, 218·2, and after standing 15¼ hrs., 263·3. G. Foussereau found that the conductivity of the aq. soln. is affected by light in that it accelerates the rate of change, but not the final state of equilibrium. Measurements were made by W. Dittenberger and R. Dietz, G. Foussereau, and F. Kohlrausch; A. Miolati observed:

v . . .	32	64	128	256	512	1024
μ Fresh . .	102·2	132·4	168·1	207·7	246·0	276·5
μ Months old .	205·0	222·5	242·0	264·4	285·1	206·2

F. Kohlrausch observed that the hydrolysis decreases rapidly with increasing concentration, and it augments two or three times the conductivity of soln. between 0·05N- and N-$PtCl_4$; he attributed the acidity and the high conductivity of soln. of platinic chloride to the formation of a complex acid, $H_2PtCl_4(OH)_2$; and this was confirmed by A. Miolati; H. T. S. Britton and E. N. Dodd represented the reaction by $PtCl_4+nH_2O \rightleftharpoons nHCl+Pt(OH)_nCl_{4-n} \rightleftharpoons (n-m)HCl+mH^{\cdot}+Pt(OH)_nCl'_{4-n+m}$. O. Stelling studied the electrolytic reduction of the acid in hydrochloric acid soln. N. Thon studied the electrolysis with a rarefied gas electrode. W. Hampe noted the conductivity of the aq. soln., and that platinum is electrolytically deposited; and that alcoholic soln. are good conductors, but ethereal soln. are bad ones. D. M. Bose and H. G. Bhar, and J. A. Christiansen and R. W. Asmussen studied the magnetic properties.

S. M. Jörgensen gave for the constitution of the pentahydrate:

$$Cl_2{=}Pt{<}\begin{matrix}Cl{=}Cl{-}H\\O{-}H\end{matrix}\,.\,4H_2O$$

G. Wyrouboff said $Pt(OH)_2Cl_2.2HCl.2H_2O$; and L. Pigeon added that all 5 mols. of water are water of crystallization because they can be removed by gradually heating the salt to 215° without interfering with the $PtCl_4$-group. Chlorine is first evolved at about 360°. S. M. Jörgensen, and F. Kohlrausch, however, showed that the fifth molecule of the pentahydrate cannot be removed without decomposing the salt. The constitution was discussed by A. Hantzsch, and A. Müller.

According to A. Miolati, the conductivity of aq. soln. of platinic chloride is characteristic of that for a weak acid, and is similar to that of selenious acid. W. Hittorf and H. Salkowsky, and W. Dittenberger and R. Dietz observed that in the electrolysis of aq. soln., platinum goes to the anode. This is taken to indicate that an oxy-acid, H_2PtOCl_4, is formed. W. Pullinger found that an aq. soln. of platinic

chloride has a marked acidic reaction towards litmus, and rapidly decomposes a soln. of sodium carbonate with the evolution of carbon dioxide. F. Kohlrausch observed that, owing to hydrolysis, the conductivity of the aq. soln. changes rapidly as time goes on, and, when the limit of the hydrolysis in dil. soln. is attained, all the chlorine is present as hydrogen chloride; in more conc. soln., the hydrolysis does not go so far. The observed data agree with the assumption that H_2PtOCl_4 is a moderately-ionized, monobasic acid. The hydrolysis is accompanied by a change in colour from an almost greenish-yellow to a bright orange-red, and in more dil. soln., there is a kind of fluorescence, which is attributed to the separation of finely-divided platinic hydroxide. A. Miolati observed that when an aq. soln. of platinic chloride is titrated with sodium hydroxide using phenolphthalein as indicator, neutralization occurs when 2 eq. of the alkali have been added. The sp. conductivities of soln. to which successive quantities of alkali have been added, showed that an acid and a normal salt were present. The presence of a dibasic acid in aq. soln. of platinic chloride is also shown when a standard soln. of ammonia is employed in the titration. Salts corresponding with the acid $H_2[Pt(OH)_2Cl_4]$, or $H_2[PtOCl_4]$, have been prepared. L. Reed observed that when a drop of an aq. conc. soln. of platinic chloride is placed on filter-paper, the double ring which is formed corresponds with the presence of two different hydrates with different rates of diffusion. A. Miolati suggested that the increase in conductivity with the age of the soln. is due to a reaction symbolized: $2H_2[Pt(OH)_2Cl_4] \rightleftharpoons H_2PtCl_6 + Pt(OH)_4Cl_2 + H_2O$; and J. Wagner explained the increase in the conductivity with the age of the soln. is due to the reactions symbolized: $H_2Pt(OH)_2Cl_4 \rightleftharpoons H_2PtOCl_4 + H_2O$; followed by $H_2PtOCl_4 = PtCl_4 + H_2O$; and by $PtCl_4 + H_2O = 2HCl + PtOCl_2$. W. Hittorf and H. Salkowsky said that the platinic chloride probably passes into soln. as the monohydrate, and that this added mol. of water causes the ready scission of the molecule. It is assumed that platinic chloride is intermediate between ordinary metallic chlorides, and those chlorides which are decomposed by water. W. D. Treadwell and M. Zürcher studied the electrometric titration of the salt.

F. C. Phillips observed that **hydrogen** reduces the solid, hydrated platinic chloride below 80° with the evolution of water and hydrogen chloride; and that an aq. soln. of the chloride is slowly but completely reduced by hydrogen in the cold, or at 100°. V. V. Ipatéeff and co-workers found that at 20° to 30°, platinum is precipitated by hydrogen under 25 to 50 atm. press. W. Pullinger, A. Rosenheim and W. Löwenstamm, A. Gutbier and F. Heinrich, and L. Pigeon noted that anhydrous platinic chloride is freely soluble in **water**, and that there remains a pale, orange-red residue which is thought to be one of the lower chlorides; A. Gutbier and F. Heinrich, and L. Pigeon found that the hydrated forms also dissolve in water—the monohydrate with the evolution of heat, and the tetra- and penta-hydrates with the absorption of heat. For the hydrolysis of the salt in aq. soln., *vide supra*. According to R. Engel, dry **hydrogen chloride** liquefies the solid tetrahydrate at 50°, forming hydrochloroplatinic acid; and S. M. Jörgensen also observed that **hydrochloric acid** immediately converts the pentahydrate into hydrochloroplatinic acid. A. Ditte observed that hydrated platinic chloride dissolves more readily in hydrochloric acid, the more concentrated the acid. D. Helbig and G. Fausti showed that hydrated platinic chloride is insoluble in liquid hydrogen chloride. F. Gramp showed that **iodine** reduces an aq. soln. of platinic chloride to platinous chloride. H. St. C. Deville and J. S. Stas, H. Rose, etc., observed that **potassium chloride,** or **ammonium chloride,** precipitates a yellow or orange, crystalline or amorphous chloroplatinate, sparingly soluble in water and acids, insoluble in alcohol. C. Claus said that potassium iodide colours a soln. of a platinic salt a deep purple-red, and a precipitate of platinic iodide then appears. The precipitation is hastened by heating the liquid. W. H. Seamon observed that potassium chloride added to a soln. containing a little iodine produces a red coloration owing to the formation of platinic iodide; if much iodine is present, a precipitate is formed. H. Peterson observed that the dark reddish-

brown coloration, produced by adding potassium chloroplatinate to a cold, conc. soln. of potassium iodide, becomes lemon-yellow when treated with sodium thiosulphate: $PtCl_4+4KI=PtI_2+I_2+4KCl$, and $I_2+2Na_2S_2O_3=2NaI+Na_2S_4O_6$, and the reactions are available for the volumetric determination of platinum. According to C. Claus, a soln. of platinic chloride is slowly coloured brownish-red by **hydrogen sulphide,** and finally, a dark brown precipitate of platinic sulphide is formed; the precipitation is more rapid in hot soln. The same precipitate is formed by ammonium sulphide, and it is soluble in a large excess of this reagent. C. T. Barfoed added that the precipitate dissolves in warm, dil. nitric acid, but not in hydrochloric acid; N. W. Fischer said that the precipitate is soluble in hydrochloric acid, and H. Reinsch observed that a soln. of 1 part of platinic chloride in 100 parts of water and mixed with 25 parts of hydrochloric acid does not give a precipitate with hydrogen sulphide. This statement suggests that there is a reversible reaction: $PtCl_4+2H_2S \rightleftharpoons PtS_2+4HCl$—**10.** 57, 9. U. Antony and A. Lucchesi found that all the metal is precipitated as platinic sulphide from a 3 per cent. aq. soln. of platinic chloride at 90°, and that for analytical purposes, the precipitate should be collected and washed in an atm. of hydrogen sulphide, and dried in an atm. of nitrogen, at 70° to 80°. At ordinary temp., 15° to 18°, a mixed yellow and brown precipitate is formed in soln. of hydrochloroplatinic acid, and the supernatant liquid remains red; the mixed precipitate continually loses hydrogen sulphide on heating, and ultimately yields platinic sulphide at 200°. The brown and yellow precipitates are possibly platinic hydrosulphides. The reddish mother-liquor contains colloidal platinic sulphide, which is slowly deposited even at 0°. A 0·5 per cent. aq. soln. of hydrochloroplatinic acid gives no precipitate at 15° to 18° with hydrogen sulphide, but only a red-brown coloration; no precipitate is obtained on boiling, but on adding hydrochloric acid, the soln. deposits platinic sulphide, and becomes decolorized. The precipitation of platinic sulphide from the more conc. soln. at 15° to 18° thus seems due to the action of the liberated hydrochloric acid. H. Schiff found that **potassium polysulphide**—or liver of sulphur—gives a precipitate which dissolves when boiled with an excess of the reagent. L. Crosnier studied the action of **metal sulphides** on platinic chloride; and A. Levallois found that when the hydrated chloride is heated with **lead sulphide,** it is decolorized, and furnishes yellow anastosmosed needles. O. Brunck found that **sodium hyposulphite** colours a soln. of platinic chloride dark red, and hydrochloroplatinous acid is formed, and some sulphur is precipitated. A soln. containing 0·1 grm. of platinum per litre is intensely coloured at once by the hyposulphite; but a soln. with 0·01 grm. per litre is coloured when warmed and viewed in a layer 10 cms. thick. G. Geitner found that **sulphurous acid** decolorizes a soln. of platinic chloride, and if the decolorized soln. be heated in a sealed tube at 200°, platinic sulphide is formed; at ordinary temp., K. Birnbaum found that platinous chloride is formed and that the chlorine of that compound can be replaced by the radicles HSO_3, $NH_4SO'_3$, etc. According to P. Berthier, a soln. of platinic chloride is very rapidly decolorized by soln. of potassium or ammonium sulphite, particularly when heated with an excess of the sulphite, a white precipitate is formed which dissolves in an excess of water particularly when heated. The precipitate formed in cold soln. is probably the chloroplatinite. J. von Liebig observed that when a soln. of hydrochloroplatinic acid is decolorized by sulphurous acid, and treated with ammonia, platinous tetramminochloroplatinite is formed—and similarly with **ammonium** or **potassium sulphite.** J. B. A. Dumas said that the anhydrous salt is insoluble in conc. **sulphuric acid;** but, according to D. Vitali, conc. sulphuric acid acts on hydrated platinic chloride with the evolution of chlorine, and the formation of a yellow precipitate. H. B. North found that the pentahydrate is sparingly soluble in **sulphuryl chloride.**

A. Smits observed that **magnesium nitride** reduces platinic chloride to the metal. G. Gore observed that platinic chloride is slightly soluble in liquid **ammonia,** and E. Divers that it dissolves and reacts with an ammonia soln. of ammonium

nitrate. W. Peters showed that anhydrous platinic chloride takes up 6 mols. of dry ammonia, and that the resulting hexammine in vacuo loses a mol. of ammonia. R. Silberberger found that the presence of platinum salts in dil. soln. does not affect the precipitation of **barium sulphate** by the addition of barium chloride; in conc. soln. some platinic salt may be adsorbed by the precipitated barium sulphate. H. Vohl, and W. Knop observed that in acidic soln. platinum salts give a precipitate of platinous sulphide when they are treated with a soln. of **sodium thiosulphate**—particularly with warm soln.; and P. Schottländer, and P. Jochum, that in ammoniacal soln., a complex platinous alkali thiosulphate is formed. M. C. Lea observed that with an ammoniacal soln. of sodium thiosulphate, ammonium chloroplatinate is first precipitated, and then, with heating, the soln. becomes yellow, then colourless, and finally wine-red. C. Langlois observed that **trithionic acid** gives a black precipitate; M. C. Lea, that **tetrathionic acid** forms a wine-red soln.; F. Raschig, that **sulphaminic acid** produces no change in a soln. of hydrochloroplatinic acid; and J. A. Palmer, that ammonium thiocarbonate in ammoniacal soln. along with ammonium chloride, gives a precipitate soluble in excess. H. Rose, M. Delépine, and G. and W. van Dam noted that with ammonia a precipitate of ammonium chloroplatinate is formed in soln. of platinic chloride, and that the precipitate is soluble in excess when heated; the precipitate is attacked by chlorine; $3Cl_2+(NH_4)_2PtCl_6=PtCl_4+8HCl+N_2$. H. St. C. Deville and J. S. Stas, S. M. Jörgensen, and S. A. Norton observed that **ammonium chloride** slowly forms a precipitate with the aq. soln. at ordinary temp. or when heated.

T. Curtius and H. Schulz represented the reaction with **hydrazine**: $2PtCl_4+N_2H_4.H_2O=2PtCl_2+4HCl+N_2+H_2O$. E. Knoevenagel and E. Ebler found that hydrazine gives a precipitate in an ammoniacal or feebly acidic soln. and **hydroxylamine** gives an incomplete precipitation in ammoniacal soln. N. Tarugi studied the reaction with hydroxylamine; and F. Reitzenstein observed that hydroxylamine gives no precipitate with a cyanide soln. H. Rose found that **potassium nitrite** precipitates potassium chloroplatinate from soln. of platinic chloride, and that boiling the soln. produces no further change. H. Precht, H. D. Rogers and M. H. Boyé observed that a soln. of platinum in **aqua regia** containing an excess of nitric acid furnishes **platinic tetrachlorobisdinitrosylchloride,** $[Pt(NOCl)_2Cl_4]$—R. Weber recommended fuming nitric acid, and gave the formula $PtCl_4.N_2O_3Cl_2.H_2O$. S. M. Jörgensen obtained it by passing the vapours from aqua regia into a conc. soln. of hydrochloroplatinic acid, and drying the crystals at 100°; and J. J. Sudborough, by the action of nitrosyl chloride on platinum at 100°. S. M. Jörgensen said that the yellowish-brown crystalline powder contains cubic forms. No water is lost at 100°, but stronger heating decomposes the salt leaving platinum behind. The crystals are very deliquescent, and freely soluble in water. The salt decomposes in aq. soln. E. Baudrimont prepared a complex with **phosphorus pentachloride,** namely, **platinic tetrachlorodiphosphorichloride,** $[Pt(PCl_5)_2Cl_4]$. R. Böttger observed that **phosphorus,** at ordinary temp., does not decompose soln. of platinum salts, but A. C. Christomanos observed that a soln. of phosphorus in ether or benzene gives a precipitate with soln. of platinic chloride. R. Böttger observed that **phosphine** does not give a precipitate with soln. of platinic salt; on the contrary, P. Kulisch found that with platinic chloride soln., phosphine gives a lemon-yellow precipitate which soon becomes darker, and finally, dark brown. R. Engel said that some platinous hypophosphite is formed. G. Oddo found that anhydrous platinic chloride is soluble in **phosphoryl chloride.** L. Vanino, A. Gutbier, and A. Gutbier and G. Hofmeier observed that **hypophosphorus acid** does not precipitate platinum. M. C. Lea, and A. Atterberg said that with **hypophosphites** platinic chloride is reduced to platinous chloride and, added A. Sieverts and M. Major, the metal is not formed in hot or cold or in acidified soln. but with very dil. soln. of potassium chloroplatinite, and a large excess (1 : 120) of a warm soln. of sodium hypophosphite. A. Sieverts and E. Peters observed that a yellowish-brown colloidal soln. of platinum is formed. A. Rosen-

heim and W. Levy observed that platinic chloride acts only on the esters of quinquevalent phosphorus and not on those of tervalent phosphorus; with ethyl phosphate, it interacts to form **triethyl phosphate platinochloride**, whilst it does not act on ethyl phosphite. Platinous chloride, on the other hand, reacts with esters of phosphorous acid, but not with esters of phosphoric acid. C. Claus, and H. Rose found that **sodium phosphate** does not give a precipitate with cold or boiling soln. of platinic chloride. B. E. Dixon studied the action of alkali phosphates on hydrochloroplatinic acid in ammoniacal soln. L. Kahlenberg and J. V. Steinle represented the reaction with **arsenic** by $3PtCl_4+4As+6H_2O=3Pt+2As_2O_3+12HCl$. J. F. Simon, and R. Bartels found that **arsine** gives a black precipitate with soln. of platinic chloride. C. Reichard observed that **potassium hydroarsenite** precipitates platinic arsenite from soln. of platinic salts; and T. Thomson, that **sodium arsenate** gives a light brown precipitate soluble in nitric acid. J. F. Simon, and R. Bartels observed that **stibine** gives a black precipitate in soln. of platinic chloride, and that the precipitate contains antimony trioxide and platinum, and possibly a platinum and antimony compound is formed. M. C. Harding found that a dil. soln. of platinic chloride, and an excess of **antimonious acid,** gives a dark brown precipitate containing platinum and antimony trioxide.

According to E. Heymann, when a soln. of platinic chloride is treated with **carbon** at room temp., hydrolytic absorption occurs; and a reduction to metallic platinum occurs at 100°. E. Heymann found that the platinum compound which is adsorbed by carbon from aq. soln. of platinic chloride, at ordinary temp., is probably a hydrolysis product, say, $Pt(OH)_4$, at 100°, platinum is adsorbed. According to G. Gore, **coal gas,** bubbled through a soln. of platinic chloride, decomposes only a very small proportion during 10 weeks; the products of combustion also produce only a slight decomposition. P. Köthner, and H. Erdmann and P. Köthner found that **ethylene,** and *iso***butylene** have no action in the cold, whilst **propylene, trimethylene,** and **acetylene** have no action in the cold or at 100°. In the replacement of chlorine atoms by hydrocarbon radicles, compounds like **platinic trimethylchloride,** $(CH_3)_3PtCl$, are formed. According to E. G. Cox and C. Webster, this compound has a body-centred cubic lattice with $a=10{\cdot}52$ A., and 8 mols. per unit cell.

F. C. Phillips observed that **carbon monoxide** acts on cold and boiling soln. of platinic chloride forming carbon dioxide; no precipitate is formed, but the soln. is reduced to platinous chloride, and if the action is continued for days or weeks, the metal is precipitated. I. Sano obtained a colloidal soln. by the action of carbon monoxide. G. Gore also obtained a yellow precipitate on passing a mixture of carbon monoxide and dioxide through a soln. of platinic chloride for 2 or 3 days. At 140°, W. Manchot and E. Enk said that platinous dicarbonyl dichloride is formed (*q.v.*).

J. Haidlen and R. Fresenius said that **potassium cyanide** with soln. of platinic chloride give a precipitate of platinic cyanide, soluble in an excess assisted by heat; the precipitate is decomposed by acids. C. Claus, and H. Rose found that unlike the palladium salt, platinic chloride does not react with **mercuric cyanide.** H. Rose observed that **potassium ferrocyanide** gives a precipitate of potassium chloroplatinate, and C. Claus, that potassium ferrocyanide gives a dark green liquid, and **potassium ferricyanide** produces a dirty brownish-green colour. C. Luckow said that no precipitation occurs with the ferrocyanide or ferricyanide and $0{\cdot}05N$-$PtCl_4$; and R. Meldrum observed no reaction with the ferricyanide in cold or hot, acidic or alkaline soln.; but the ferrocyanide produces a precipitate in 1 per cent. soln. and the precipitate becomes dark green when boiled, and it is blackened by ammonia; a 0·2 per cent. soln., when boiled with a few drops of the ferrocyanide, gives a dark green, almost black, coloration. When boiled with an excess of the ferrocyanide, a green precipitate is formed which becomes olive-green and finally yellow when it is treated with ammonia; the addition of more ferrocyanide produces a yellow soln. The green precipitate dissolves in hydrochloric

acid to give an indigo-blue soln., and this reaction enables 1 part of platinum in 1000 parts of soln. to be detected. D. Vitali noted that in ammoniacal soln. of platinum chloride potassium ferrocyanide and ferricyanide give yellow precipitates of potassium chloroplatinate, with a red soln. in the former case, and a green soln. in the latter case. E. H. Miller and J. A. Mathews, and F. van Dyke Cruser and E. H. Miller observed that **potassium cobalticyanide** gives no precipitate with 10 per cent. soln. of hydrochloroplatinic acid or sodium chloroplatinate. C. Claus, and H. Rose said that **potassium thiocyanate** darkens a soln. of platinic chloride owing to the formation of a very soluble thiocyanate. The reaction was studied by G. B. Buckton. F. W. Clarke and M. E. Owens found that an alcoholic soln. of platinic chloride gives a pale buff precipitate with **potassium cyanate.**

A. E. Dunstan, and A. E. Dunstan and L. Cleaverley observed that **benzoflavol** forms a complex salt: $(C_{21}H_{17}O_2N)_4H_2PtCl_6$; G. T. Morgan and F. M. G. Micklethwait obtained a complex with **cumarin,** $(C_{36}H_{24}O_8)H_2PtCl_6.4H_2O$; A. von Baeyer and V. Villiger, with **cinnamaldehyde,** and **benzylideneacetone ;** and A. Rosenheim and co-workers, with **ethylacetoacetate,** and **acetylacetone.** According to F. C. Phillips, **carbonyl sulphide** gives a black coloration with platinic chloride; **methyl hydrosulphide,** a yellowish-brown precipitate, and **methyl sulphide,** a pale yellow precipitate, which, according to P. C. Ray and P. C. Mukherjee, is $PtCl_3.2(CH_3)_2S$. M. Delépine observed that a precipitate is produced by soln. of **thiocarbamates.** A. W. Hofmann studied the action of **thioacetamide,** and A. Behal and E. Choay, the action of **chloralimide.** C. Vincent observed that **dimethylamine** gives an orange-yellow precipitate with conc. soln. of platinic chloride ; **trimethylamine,** a yellow precipitate ; and **dipropylamine,** no precipitate. G. Martina observed no precipitation with **phenylhydrazine.** W. Hampe found that the salt is slightly soluble in dry **ether,** and also in absolute **alcohol.** A. Rosenheim and W. Löwenstamm, W. Eidmann, and W. C. Zeise found that platinic chloride is soluble in **alcohol.** P. Schützenberger evaporated a soln. of platinic chloride in absolute alcohol at ordinary temp. in vacuo over sulphuric acid and obtained **platinic tetrachlorobis-ethylalcoholate,** $[Pt(C_2H_5OH)_2Cl_4]$. E. Biilmann observed that **allyl alcohol** does not reduce boiling soln. of platinic chloride. W. C. Zeise observed that platinic chloride is soluble in **ether,** but A. Rosenheim and W. Löwenstamm, and R. Willstätter said that it is insoluble in ether. F. Mylius and C. Hüttner observed that when ether is shaken up with an aq. soln., only a trace of platinic chloride dissolves in the ethereal layer. W. C. Zeise, W. Eidmann, A. Rosenheim and co-workers, and A. Naumann found that anhydrous platinic chloride is soluble in **acetone ;** A. Rosenheim and W. Löwenstamm, soluble in **acetylacetone ;** and A. Naumann, slightly soluble in **methyl acetate.** C. Claus, and H. Rose observed no reaction between **lead acetate** and soln. of platinic chloride ; H. Rose, that **oxalic acid** gives no precipitate ; C. Claus, that **tannin** acts neither in cold nor in hot soln. ; K. A. Hofmann and D. Strom, that **tetraformaltrisazine** gives an intense yellow coloration ; A. C. Neish, that *m*-**nitrobenzoic acid** gives no precipitation ; and M. Wunder and V. Thuringer, that **dimethylglyoxime** is not a suitable precipitant for quantitative work. E. Beckmann and W. Gabel reported the hydrated chloride to be soluble in **quinoline.** W. D. Bancroft found that platinic chloride gives a precipitate with **gelatin,** but not with **agar-agar ;** K. Kruis, that **aniline black** is fixed on fibres by platinic chloride ; J. Murray, that blue **vegetable colours** are turned green by platinic chloride ; and V. Martinand, that a soln. of platinic chloride acts catalytically like an oxydase. E. Wedekind observed that a colloidal soln. of **zirconium silicide** gradually produces a precipitate with soln. of platinic chloride ; and C. Claus, that **borax** does not give a precipitate in cold or in boiling soln. E. Müller and W. Stein titrated the soln. electrometrically with **titanous chloride.**

F. Reitzenstein observed that **sodium amalgam** does not react with cyanide soln. of platinum salts, and similarly also with **zinc** dust. O. Loew found that hydrochloroplatinic acid and **zinc amalgam** form mercury hydride. G. and W. van

Dam observed that a drop of **mercury** causes the evolution of ammonia from soln. of platinic alkylaminochlorides. A. Merget studied the action of mercury vapour. F. Mylius and O. Fromm found that **tin** gave a black or yellowish-brown precipitate; and **lead** precipitates a platinum-lead alloy. H. Rose observed that soln. of platinic chloride with **potassium hydroxide** give a precipitate of potassium chloroplatinate, which dissolves if a large excess of alkali is present, and the mixture is warmed. F. Reitzenstein observed that **sodium hydroxide** gives no precipitate in cyanide soln. of platinum salts. D. Vitali observed that **silver oxide** decomposes soln. of platinic chloride completely. According to H. Rose, **potassium carbonate** or **hydrocarbonate** gives a precipitate with soln. of platinic chloride, and the precipitate is insoluble in an excess; **sodium carbonate** does not give a precipitate at ordinary temp., but with a prolonged boiling sodium platinate is formed; **calcium hydroxide** forms a yellowish-white precipitate, especially in sunlight, and barium carbonate gives no precipitate in the cold or with boiling soln. J. F. W. Herschel studied the action of lime-water on the soln. exposed to light. W. Kwasnik found that **barium dioxide** reduces a mixture of platinic chloride and silver chloroplatinate to metal, but not so with hydrochloroplatinic acid. K. Birnbaum noted that **silver chloride** is readily dissolved in conc. soln. of platinic chloride, as nearly neutral as possible, but is recovered unchanged on evaporating the soln. C. Claus, and A. Commaille observed that **silver nitrate** gives a yellow precipitate of silver chloroplatinite. F. W. Clarke found that with **silver fluoride** there is a reaction: $PtCl_4+4AgF+2H_2O=PtO_2+4AgCl+4HF$, and with silver nitrate some nitric acid is formed. H. Gerresheim observed that with a soln. of **Millon's base,** HgOH.NH.HgCl, in hydrochloric acid, ammonium chloroplatinate is precipitated. C. Claus, and A. Commaille observed a reddish precipitate with **mercurous nitrate** soln. C. T. Barfoed observed that **stannous chloride** colours soln. of platinic salts a deep reddish-brown, and after a time the soln. is decolorized as a gelatinous precipitate is formed. R. Ruer observed that with conc. soln. the precipitate is brown, and with very dil. soln., it is yellow; and G. A. Hulett obtained yellow colorations with very dil. soln. L. Wöhler and A. Spengel found that the red colour is developed by the presence of ether, or better still, of ethyl acetate; it is not conditioned by the formation of platinous chloride, but rather by the formation of colloidal platinum—*vide* purple of Cassius—**3.** 23, 11; **7.** 46, 14. E. Müller and W. Stein titrated the soln. electrometrically with stannous chloride. M. Frenkel said that no precipitate is produced by **potassium chromate** in soln. of platinic chloride. O. W. Gibbs obtained a series of complex platinic molybdates by the action of platinic chloride on soln. of **ammonium molybdate;** and complex platinic tungstates, when **sodium tungstate** is used. F. W. O. de Coninck observed that dil. soln. of **uranous sulphate** and manganous sulphate do not act on soln. of chloroplatinates in darkness or in diffuse daylight; in sunlight, the uranous sulphate is oxidized to uranic sulphate, and a basic sulphate whilst platinous chloride is formed. A mixture of **manganous chloride** and platinic chloride gave no precipitate after standing 6 months. E. H. Miller found platinic chloride useful as an external indicator in the titration of manganese or zinc salts with potassium ferrocyanide; it furnishes an emerald-green coloration. J. Wagner observed that the reaction between **permanganate** and an oxalate is accelerated by platinic chloride. J. Murray observed the decomposition of platinic chloride by **magnetized iron.** H. Rose said that **ferrous sulphate** does not act on soln. of platinic chloride or sulphate even after a long time, but some reduction occurs with the nitrate. R. Chenevix, and H. Rose found that a mixture of platinic and mercuric chlorides is slowly reduced by ferrous sulphate, but rapidly if some platinous chloride is also present. R. W. Mahon employed a soln. of platinic chloride containing 0·05 grm. of platinum per litre and 34 grms. of mercuric chloride as indicator in the titration of iron by stannous chloride. The latter in the presence of this soln. reduces the iron to the ferrous state, and then precipitates a dark cloud of mercurous chloride mixed with platinum.

W. J. Pope and S. J. Peachey prepared **trimethyl platinic chloride,** $(CH_3)_3PtCl$, by the action of hydrochloric acid on the hydroxide ; or by treating the chloride or sulphate with potassium chloride.

L. Pigeon reported that a mass of reddish-brown crystals of **hydropentachloroplatinic acid,** $HCl.PtCl_4.2H_2O$, or $HPtCl_5.2H_2O$, is formed when the hexahydrate of hydrohexachloroplatinic acid is heated in vacuo in the presence of potassium hydroxide for 2 or 3 days on a water-bath. The heat of formation ($PtCl_4$, $HCl.2H_2O$) =10·46 Cals. A. Miolati and I. Bellucci considered that the alleged hydropentachloroplatinic acid is really hydroxypentachloroplatinic acid, $H_2Pt(OH)Cl_5$—*vide infra.*

According to L. Pigeon, if conc. sulphuric acid be added to a cold, conc., hydrochloric acid soln. of platinic chloride, yellow, crystalline **hydrohexachloroplatinic acid,** or simply **hydrochloroplatinic acid,** $H_2PtCl_6.4H_2O$, is precipitated. The *tetrahydrate* can be filtered off and dried on porcelain tiles. The ordinary form of this acid is the *hexahydrate*, $H_2PtCl_6.6H_2O$. R. Engel showed that the decahydrated platinic chloride of C. H. D. Bödeker, H. Lawrow, and M. Protopoff is probably the hexahydrated acid—*vide supra.* S. M. Jörgensen, R. Engel, and L. Pigeon made some observations on the constitution. L. F. Nilson represented it by $(H.Cl : Cl)_2{=}Pt{=}Cl_2.6H_2O$; R. Engel, $(PtCl_4.2H_2O)2(HCl.2H_2O)$; and L. Pigeon, $PtCl_4(HCl.2H_2O)_2.2H_2O$. J. J. Berzelius showed that the aq. soln. reacts acidic to litmus. J. Thomsen showed that the acid is dibasic, and forms double salts with the bases. The heats of neutralization of an eq. of the acid with 2, 4, and 6 eq. of NaOH—namely, 27·216, 27·240, and 27·336 Cals.—are characteristic of strong acids. P. Klason, and P. Walden also showed that the properties of the soln. agree with the dibasicity of the acid. L. Spiegel discussed the electronic structure.

An aq. soln. of hydrochloroplatinic acid was prepared by N. A E. Millon, by dissolving spongy platinum in conc. aqua regia, the excess of nitric acid can be removed by successive additions of hydrochloric acid and evaporations. The presence of a trace of nitrous acid is necessary for the dissolution of the platinum. A mixture of nitric acid, free from nitrous acid, and potassium chlorate has no action on spongy platinum even at 125° ; nor is spongy platinum attacked by a cold mixture of sufficiently-diluted hydrochloric acid and purified nitric acid, but the attack proceeds slowly on adding potassium nitrite. H. D. Rogers and M. H. Boyé said that a platinic nitrosylchloride is formed if a very large excess of aqua regia is employed, and R. Weber, if fuming nitric acid be used. The excess of nitric acid was removed by R. Weber, F. Stolba, etc., by repeated evaporation with hydrochloric acid.

K. Seubert recommended cleaning platinum scraps with boiling hydrochloric acid, and then dissolving them in aqua regia contained in a large flask, and kept warm for about 3 days. The soln. was then evaporated to free it from the excess of nitric acid ; soda-lye added until the soln. reacts alkaline ; and the liquid boiled for a long time to decompose the hypochlorites ; some alcohol added, then hydrochloric acid, and the mixture filtered to remove the olive-green precipitate which was mainly iridium chloride. The platinum was precipitated as ammonium chloroplatinate, ignited, and the residue boiled several times with dil. hydrochloric acid, then washed by decantation with hot water, and the residue digested with aqua regia, diluted with 2 vols. of water, and kept warm on a water-bath for 12 hrs. The soln. was evaporated in a slow current of chlorine, with frequent additions of hydrochloric acid to drive off the nitric acid.

L. Pigeon, and W. Dittmar and J. McArthur dissolved the spongy platinum in hydrochloric acid through which a current of chlorine was passed for 12 hrs. The excess of chlorine was removed from the clear liquid by evaporation. E. V. Zappi dissolved platinum in a mixture of conc. hydrochloric and chloric acid. P. Rudnick, and P. Rudnick and R. D. Cooke oxidized with conc. hydrogen dioxide. H. C. P. Weber obtained a soln. of hydrochloroplatinic acid by dissolving spongy or scrap platinum in aqua regia, removing the excess of acid by neutralization or evaporation, and reducing the soln. with alkali formate or zinc. The precipitated

platinum is warmed with a little dil. hydrochloric acid in order to remove iron, and is then transferred to the electrolytic apparatus, where it is washed and afterwards covered with conc. hydrochloric acid. The electrodes are composed of sheet platinum. The precipitated platinum thus forms the anode of an electrolytic cell. On concentrating the soln. of hydrochloroplatinic acid resulting from the electrolysis, a small quantity of chlorine is introduced in order to ensure the absence of platinous compounds. H. Precht described the preparation of hydrochloroplatinic acid from platinum residues. L. N. Vauquelin passed chlorine into warm water containing ammonium chloroplatinate in suspension until all the ammonia is decomposed—there is here a possibility of forming explosive nitrogen chloride. L. Pigeon employed this process.

On slowly evaporating the soln. of hydrochloroplatinic acid prepared by one of these processes—say over calcium oxide and conc. sulphuric acid as recommended by R. Weber—brownish-red, deliquescent crystals of the hexahydrate are formed. H. W. Hake said that the maximum quantity of water absorbed during a few days' exposure to atmospheric air amounts to 47·82 per cent.—*i.e.* $H_2PtCl_6.21H_2O$. R. Engel said that the salt is relatively stable. When heated, it loses hydrogen chloride and water, and then some chlorine is given off and platinous chloride is formed. H. Töpsöe observed that some hydrogen chloride, and chlorine are lost at 110°, and, added J. J. Berzelius, at a higher temp., platinous chloride and platinum are formed. According to L. Pigeon, no platinous chloride is formed when the hydrochloroplatinic acid is heated 5 hrs. in vacuo at 170°; at 280°, a small proportion of platinous chloride is formed, but more is produced at 358°. When heated in vacuo in the presence of potassium hydroxide, the first product of the action is $HPtCl_5.2H_2O$, and afterwards platinous chloride appears. The heat of formation $(2HCl.6H_2O, PtCl_4)$=20·46 Cals., $(HCl.4H_2O, HPtCl_5.2H_2O)$ =10·00 Cals., and $(PtCl_4, 2HCl)$=24·8 Cals.; the heat of soln. is 4·34 Cals. J. Thomsen gave (Pt, Cl_4, 2HCl, Aq.)=84·62 Cals.; (Pt, O_2, 6HCl, Aq.)=64·06 Cals. Y. Shibata and K. Harai, and R. Samuel and A. R. Despande studied the absorption spectrum.

K. Seubert said that the aq. soln. of the purified salt is golden-yellow, and J. J. Berzelius added that if some iridium salt is present, the colour may be reddish-yellow, or brown. According to A. Hantzsch, eq. soln. of hydrochloroplatinic acid and of sodium chloroplatinate, containing the complex $PtCl_6''$-ion, in the same solvent, are optically identical—that is, they show the same absorption spectrum, and the molecular absorption is independent of the degree of ionization. The light absorption of the acid and of the salt is also unaffected by changes of temperature. The solvent does not appear to exercise any influence on the absorption in the blue and violet parts of the spectrum, but does so to a very slight extent in the green and ultra-violet. The temp. coeff. of the absorption spectrum is very small. F. Kohlrausch observed that the behaviour of soln. of hydrochloroplatinic acid in light resembles that of soln. of platinic chloride—*vide supra.*

The electrical conductivity of soln. of $0·1N$-H_2PtCl_6 changes in light owing to hydrolysis; but more conc. soln. are stable, and are not affected by light. A freshly-prepared soln. with 0·0002 gram-equivalent per litre had an eq. conductivity 380, and when hydrolyzed in light, 1048, showing that all the chlorine is probably present as hydrochloric acid. J. A. Prins and A. Fonteyne studied the X-ray diffraction of aq. soln. The eq. conductivities, λ, of soln. of the following concentration in gram-equivalents per litre, at 18°, were:

	0·0002*N*-	0·001*N*-	0·002*N*-	0·01*N*-	0·1*N*-	0·37*N*-	0·88*N*-	2·65*N*-
λ Not insolated	380	367	362	352	325	302	265	155
λ Insolated	1048	1036	776	365	—	—	—	—

F. Braun succeeded in converting up to 49 per cent. of the heat of combination into electrical energy. S. Nagami measured the lowering of the f.p., the ionic

mobility, migration velocities, and the effect on the hydrolysis of acetates. The eq. electrical conductivities of soln. with an eq. of the acid in v litres, at 25°, are :

v	10	50	100	1000	10,000
λ	366·1	384·3	395·5	409·6	418

M. Boll, and M. Boll and P. Job also studied the conductivity of 0·0001N-soln. of hydrochloroplatinic acid exposed to light, and the results show that in every case an atom of chlorine remains combined with the platinum ; they suggested that the compound formed will probably contain two atoms of platinum in the molecule since the monoplatinic acids are unstable under the given conditions; the hydrolysis may be represented by the equation : $2H_2Pt(OH)_{6-n}Cl_n+(2n-1)H_2O=(2n-1)HCl+H_2Pt(OH)_5Cl.H_2Pt(OH)_6$, where n may be 1, 2, 3, 4, 5, or 6. The soln. obtained remain unaltered for a time, but finally deposit a reddish-brown, flocculent precipitate of platinic hydroxide: $H_2PtCl(OH)_5.H_2Pt(OH)_6+H_2O=HCl+2H_2Pt(OH)_6$; and there is a further increase in conductivity. M. Boll observed that the hydrolytic changes which occur in the dark with very dil. soln. of hydrotetrachloroplatinic acid at temp. between 10° and 100° are the same as those taking place in light, or under the influence of high-frequency rays. O. Stelling studied the electrolytic reduction of hydrochloroplatinic acid in a soln. of hydrochloric acid ; and G. Grube and co-workers studied the equilibrium : $2H_2PtCl_4 \rightleftharpoons H_2PtCl_6+Pt+2HCl$ at 60°. The value of E at 60° for $PtCl_4''$: $PtCl_6''$ is 0·745 volt ; for Pt : $PtCl_6''$, 0·765 volt ; and Pt : $PtCl_4''$, 0·785 volt.

P. Vallet said that reduction by hydrogen commences at 100°. W. Kwasnik found that barium dioxide gives a precipitate containing barium, platinum, and chlorine, and the filtrate, on evaporation, yields barium chloroplatinate. H. Töpsöe observed that hydrochloroplatinic acid is not decomposed by hypochlorous acid. The soln. of hydrochloroplatinic acid is decolorized by sulphur dioxide, or by ammonium or potassium sulphites, forming a soln. of hydrochloroplatinous acid—the reaction was studied by J. von Liebig, and P. Berthier. For the action of ammonia, *vide infra*, the ammines. O. Brunck observed that soln. of hydrochloroplatinic acid are reduced to hydrochloroplatinous acid, when they are treated with sodium hyposulphite. The dark red coloration has been recommended as a qualitative test for the metal. P. Schützenberger and C. Fontaine obtained a combination of platinic and phosphorous chlorides, **platinic tetrachlorophosphorotrichloride,** $[Pt(PCl_3)Cl_4]$, by warming the compound with platinous chloride, $[Pt(PCl_3)Cl_2]_2$, in a current of chlorine. E. Baudrimont obtained **platinic tetrachlorobisphosphoripentachloride,** $[Pt(PCl_5)_2Cl_4]$, by dissolving spongy platinum in hot phosphorus pentachloride. The ochre-yellow product fumes in air, decomposes over 300°, and it is decomposed by water. Ammonia does not form ammonium chloroplatinate. J. Thomsen said that hydrochloroplatinic acid is not decomposed by sodium hydroxide ; and W. Kwasnik, that barium dioxide forms barium chloroplatinate. The action of silver nitrate was represented, by S. M. Jörgensen, by the equations : $2HCl.PtCl_4+2AgNO_3=2AgCl.PtCl_4+2HNO_3$ in cold soln., and by $2HCl.PtCl_4+4AgNO_3+H_2O=2AgCl+2AgCl.PtOCl_2+4HNO_3$, or $2HCl.PtCl_4+4AgNO_3+2H_2O=2AgCl.Pt(OH)_2Cl_2+4HNO_3$ in hot soln. The reaction was studied by A. T. Cahours, A. Commaille, J. B. A. Dumas, R. Engel, A. F. de Fourcroy, W. Hittorf and H. Salkowsky, A. Miolati, S. A. Norton, L. Pigeon, and L. N. Vauquelin. H. Saha and K. N. Choudhury found that a dil. soln. of hydrochloroplatinic acid gives a precipitate of $NH_2.HgCl.PtCl_4$ when treated with Millon's salt, NH_2HgCl, in ammonia soln. According to P. Schützenberger, when a soln. of the dehydrated hydrochloroplatinic acid in absolute alcohol is evaporated in vacuo, it deposits crystals of $[Pt(C_2H_5OH)_2Cl_4]$. A. Sieverts and H. Brüning found that in the reduction of a mol. of hydrochloroplatinic acid in cold soln., 2 mols. of formaldehyde are required, and 1 mol. in hot soln. The formaldehyde is oxidized to formate in the first case and to carbonate in the second. Quadrivalent platinum is reduced to bivalent platinum by formic acid, but further

reduction proceeds very slowly except in the presence of carbonate. Platinum black prepared by reduction with an excess of sodium formate retains sodium formate very tenaciously. If the ratio HCOONa : H_2PtCl_6 is less than 2 : 1, the black is mixed with hydroxide and gives off oxygen when heated ; gas-free platinum black is produced when the ratio is just 2 : 1, and the product is grey, and not finely-divided. An excess of formate is required for finely-divided metal. E. Pace prepared a double salt with cocaine and hydrochloroplatinic acid ; and R. Fricke and F. Ruschhaupt, double salts with benzamide, and with acetamide.

The salts of hydrochloroplatinic acid, with $PtCl_6$ as a bivalent radicle, are **chloroplatinates.** L. F. Nilson arranged the chloroplatinates in groups typified by : $2R'Cl.PtCl_4$, $R''Cl_2.PtCl_4$, $R'''Cl_3.PtCl_4$, and $R''''Cl_4.PtCl_4$. F. Morges, and P. Walden showed that they are simple salts with the $PtCl_6$ as a bivalent radicle, and are not double salts. The general properties were studied by P. Rohland ; and the relation stabilities of the halogenoplatinates, by H. I. Schlesinger and R. E. Palmateer. O. Stelling studied the electrolytic reduction of the hydrochloric acid soln. M. Delépine and P. Boussi studied the dehydration of the chloroplatinates, but obtained no evidence of the presence of polymerized water molecules.

According to W. Peters,[2] when anhydrous platinic chloride is exposed to the action of dry ammonia, it takes up 6 mols. to form **platinic hexamminotetrachloride,** $[Pt(NH_3)_6]Cl_4$. This compound loses a mol. of ammonia in vacuo, but takes it up again in an atm. of ammonia. B. Gerdes obtained this hexammine by adding hydrochloric acid to a soln of the carbonate in dil. soda-lye. The nature of the salt was discussed by S. H. C. Briggs, P. Klason, and J. A. N. Friend. According to B. Gerdes, the white acicular crystals gradually pass into amber-yellow rhombohedra. They are stable at 110°, and readily soluble in water. A. Werner and A. Miolati found the mol. conductivities of soln. with a mol of the salt in 250, 500, 1000, and 2000 litres to be, respectively, 432·5, 483·9, 522·9, and 553·5. G. Beck, and I. I. Tscherniaeff and S. I. Chorunshenkoff studied the ionization constants ; and A. A. Grünberg and G. P. Faermann, the acidity of the salts. A. A. Grünberg, and G. Schwarzenbach gave for the effects of acidifying the platinum hexammines: $[Pt(NH_3)_6]^{4+} \rightleftharpoons [Pt(NH_3)_5.(NH_2)]^{3+} + H^+ = -0.55$ volt ; and $[Pt(NH_3)_5(H_2O)]^{4+} \rightleftharpoons [Pt(NH_3)_5(OH)]^{3+} + H^+ = -0.23$ volt. B. Gerdes observed that platinic and auric chlorides gave sparingly soluble precipitates. That produced by the former is the *dihydrate*, $[Pt(NH_3)_6]Cl_4.2H_2O$, which furnishes yellow octahedra which lose their water at 120°, and become paler in colour.

O. Carlgren and P. T. Cleve prepared **platinic dihydroxytetramminochloride,** $[Pt(NH_3)_4(OH)_2]Cl_2$, by the action of 3 per cent. hydrogen dioxide on platinous tetramminochloride ; and by the action of barium chloride on the corresponding sulphate. L. A. Tschugaeff and W. Chlopin found that this compound is formed by the action of hydrogen dioxide on platinous *cis*-dichlorodiammine. O. Carlgren and P. T. Cleve said that the aq. soln. furnishes colourless, monoclinic plates which K. Johansson found to have the axial ratios $a : b : c = 1.5310 : 1 : 0.6702$, and and $\beta = 100° 34'$; the (110)-cleavage is incomplete. A. Werner, and A. Werner and A. Miolati found the mol. conductivity of soln. with a mol of the salt in 125, 250, and 500 litres at 20° to be, respectively, 204·9, 218·8, and 225·7. O. Carlgren and P. T. Cleve found that 100 parts of cold water dissolve 0·485 part of the salt, and boiling water, 2·04 parts. Hydrochloric acid precipitates platinic dichlorotetramminochloride from the soln.

The product obtained by W. Peters by keeping the hexammine in vacuo is possibly **platinic chloropentamminochloride,** $[Pt(NH_3)_5Cl]Cl_3$; and L. A. Tschugaeff and N. Vladimiroff, and L. A. Tschugaeff and W. Chlopin obtained it by the action of ammonia and ammonium carbonate on platinous *trans*-dichlorodiammine. A. A. Grünberg and G. P. Faermann discussed the acidity of the salt. L. A. Tschugaeff, and L. A. Tschugaeff and W. Chlopin also prepared **platinic chloropentamminochloroplatinate,** $[Pt(NH_3)_5Cl]Cl.PtCl_6.2H_2O$; **platinic hydroxypentamminochloride,**

$[Pt(NH_3)_5(OH)]Cl_3.H_2O$, in colourless, rhombic plates; and **platinic chloroamidotetramminochloride,** $[Pt\{NH_4(NH_2)Cl\}]Cl_2$; L. A. Tschugaeff and N. Vladimiroff prepared **platinic chloropentamminohydroxide,** $[Pt(NH_3)_5Cl](OH)_3$—*vide infra*, the carbonate. A. Werner reported **platinic hydroxyaquochlorotetramminochloride,** $[Pt(NH_3)_4(H_2O)(OH)]Cl_3$, to be formed by the action of conc. hydrochloric acid on the dihydroxytetrammine. It loses hydrogen chloride in air, and with a small proportion of water deposits the dihydroxytetrammine, but with a large proportion of water it forms a soln. with an acidic reaction. I. I. Tscherniaeff and A. N. Fedorova studied the pentammines containing ethylenediamine. When platinous ethylenediaminodioxamminodichloride is treated with chlorine it forms the trans-salt of platinic dichloroethylenediaminodiamminochloride, and when this salt is treated with ammonia, it forms **platinic chloroethylenediaminotriamminochloride,** $[Pt\ en(NH_3)_3Cl]Cl_3$.

J. Gros prepared **platinic dichlorotetramminochloride,** $[Pt(NH_3)_4Cl_2]Cl_2$, by evaporating the corresponding dry nitrate with an excess of conc. hydrochloric acid, or by adding hydrochloric acid or an alkali nitrate to a soln. of the corresponding nitrate. M. Raewsky obtained it by passing chlorine into a conc., boiling soln. of platinous tetramminochloride—by using a cold soln., and drying the product at 150°, the *monohydrate* was formed; C. Gerhardt, by boiling platinic tetrachlorodiammine, with aq. ammonia, and also by treating the hydroxychlorotetramminonitrate with hydrochloric acid; O. Carlgren and P. T. Cleve, by treating a soln. of dihydroxytetramminosulphate, acidified with hydrochloric acid, with barium chloride; and A. Cossa, by mixing boiling soln. of 4·14 grms. of platinic chloride in 100 c.c. of water, and 8·67 grms. of platinous tetramminochloride in 350 c.c. of water—the product is mixed with some $[Pt(NH_3)_4]PtCl_4$. N. S. Kurnakoff, I. I. Tscherniaeff and co-workers, H. and A. Euler, W. Odling, C. Weltzien, S. H. C. Briggs, C. Grimm, and J. A. N. Friend discussed the nature of this compound. This salt is a white, or pale yellow crystalline powder, and by slowly cooling a boiling soln., J. Gros obtained regular, octahedral crystals. A. Werner and A. Miolati found the mol. conductivities of soln. of a mol of the salt in 1000 and 2000 litres of water to be, respectively, 228·9 and 240·6; and G. Bredig gave 54·3 for the velocity of migration of the $\frac{1}{2}[Pt(NH_3)_4Cl_2]''$-ion at 25°. E. Rosenbohm studied the magnetic susceptibility. A. A. Grünberg and G. P. Faermann discussed the acidity of the salt.

C. Grimm observed that platinic dichlorotetramminochloride is almost insoluble in cold water, and sparingly soluble in boiling water. A. R. Klien studied the action of water, acids, and alkaline soln. J. Thomsen, and H. and A. Euler observed that when hydrogen sulphide is passed through water with the salt in suspension, sulphur is precipitated and platinous tetramminochloride is formed. H. and A. Euler observed that warm, conc. sulphuric acid converts platinic dichlorotetramminochloride into the dichloro-sulphate; and an excess of nitric acid yields the corresponding nitrate. J. Gros found that with molten potassium hydroxide, ammonia is developed, and there remains platinum mixed with potassium chloride; P. T. Cleve also observed that the salt forms an orange-red soln. with conc. potash-lye, and ammonia is developed; when this soln. is boiled it becomes pale yellow and deposits potassium chloride on cooling, and when the soln. is treated with water, white flecks, free from chlorine, are precipitated, and when the precipitate is heated it detonates. C. Grimm, J. Gros, and H. and A. Euler found that silver nitrate precipitates from the soln. about half the chlorine as silver chloride; and C. Gerhardt observed that with a small excess of silver nitrate and a few minutes' boiling, the reaction can be symbolized: $[Pt(NH_3)_4Cl_2]Cl_2+3AgNO_3+H_2O=[Pt(NH_3)_4(OH)Cl](NO_3)_2+3AgCl+HNO_3$. L. A. Tschugaeff prepared **platinic amidochlorotetramminochloride,** $[Pt(NH_3)_4(NH_2)Cl]Cl_2$.

J. Reiset treated platinous tetramminochloride with an excess of platinic chloride and obtained **platinic dichlorotetramminochloroplatinite,** $[Pt(NH_3)_4Cl_2]PtCl_4$; he obtained the same salt by crystallization from a soln. of platinous tetram-

minochloroplatinite in a boiling soln. of platinic chloride; P. T. Cleve, by mixing boiling soln. of platinic dichlorotetramminochloride and potassium chloroplatinite; P. T. Cleve, and A. Cossa, by mixing soln. of platinic chloride and of platinous tetramminochloride; and C. Gerhardt, by the action of chlorine on platinous tetramminochloroplatinate. The reddish-brown, crystalline powder is sparingly soluble in water; and with silver nitrate, it precipitates silver chloride, and forms platinic hydroxychlorotetramminonitrate. C. Gerhardt obtained **platinic dichlorotetramminochloroplatinate,** $[Pt(NH_3)_4Cl_2]PtCl_6$, by passing chlorine into water with platinous tetramminochloroplatinite in suspension; C. Grimm, by passing chlorine into a soln. of platinous tetramminochloride; and P. T. Cleve, by mixing sodium chloroplatinate with platinic dichlorotetramminonitrate. The crystals are quadratic plates or octahedra, with the colour of potassium dichromate; they do not lose weight at 100°; and when boiled a short time with silver nitrate, precipitate three-quarters of the contained chlorine as silver chloride.

E. A. Hadow prepared **platinic hydroxychlorotetramminochloride,** $[Pt(NH_3)_4(OH)Cl]Cl_2$, by mixing a hot conc. soln. of the corresponding nitrate with an excess of ammonium chloride; he considered it to be a hemihydrate, but P. T. Cleve observed that the salt is anhydrous when dried at 100°. C. W. Blomstrand, P. T. Cleve, and W. Odling discussed the constitution. The snow-white precipitate consists of rhombic prisms, sparingly soluble in water.

P. T. Cleve obtained **platinic trichlorotriamminochloride,** $[Pt(NH_3)_3Cl_3]Cl$, in pale yellow, rhombic or hexagonal plates by boiling platinous nitratotriamminonitrate with aqua regia, and drying the crystalline product at 100°. A. Werner and A. Miolati found that the mol. conductivities of soln. of a mol of the salt in 500, 1000, and 2000 litres are, respectively, 91·43, 96·75, and 106·5. The conductivity of the first-named soln. changed to 97·5 in 3 hrs. and to 106·5 in 24 hrs.

C. Gerhardt prepared **platinic** *trans*-**tetrachlorodiammine,** $[Pt(NH_3)_2Cl_4]$, by passing chlorine into boiling water with platinous *trans*-dichlorodiammine in suspension until the pale yellow salt becomes lemon-yellow and a drop of the liquid forms yellow crystals on cold glass. C. Grimm employed a similar process, and P. T. Cleve, and W. Odling employed aqua regia or potassium permanganate as oxidizing agents in place of chlorine; and L. A. Tschugaeff and W. Chlopin, ozone in hydrochloric acid soln. S. M. Jörgensen oxidized a boiling hydrochloric acid soln. of platinous *trans*-bispyridinediamminochloride with potassium permanganate, and allowed the soln. to cool slowly. W. Lossen, and H. Alexander obtained the salt as a by-product in the preparation of hydroxylamine hydrochloride in the mother-liquor remaining after the removal of ammonium chloride by platinic chloride; and F. Hoffmann observed that it is formed when platinic *cis*-dihydroxylaminediamminochloride is boiled with hydrochloric acid. The nature of the compound was discussed by E. Gapon, C. Weltzien, C. Gerhardt, W. Odling, S. H. C. Briggs, S. M. Jörgensen, and A. Werner and co-workers. The lemon-yellow, crystalline powder consists of octahedral or quadratic plates. According to E. G. Cox and G. H. Preston, the crystals of the α-salt are lemon-yellow, tetragonal—sometimes bipyramids—usually tabular on the (001)-face; and the X-radiograms corresponded with a cell having $a=5{\cdot}72$ A., $c=10{\cdot}37$ A., and 2 mols. per unit cell, so that the calculated sp. gr. is 3·61, and the observed result is 3·3. Each ammonia group in the cell is surrounded by 8 chlorine atoms, belonging to its own or adjoining molecules, and each chlorine atom is surrounded by 4 ammonia mols. The β-salt forms lemon-yellow rhombic plates tabular on the (010)-face and bounded by the (101)-face or the (100)-face. The crystals are sometimes distorted. The cell dimensions are $a=10{\cdot}0$ A., $b=11{\cdot}2$ A., and $c=6{\cdot}0$ A. There are four molecules per unit cell, and the calculated sp. gr. is 3·6, when the found value is 3·3. P. T. Cleve observed that the crystals begin slowly to decompose at 200° to 216°, and F. Hoffmann added that no explosion occurs. E. Petersen observed that a mol of the salt dissolved in 250 litres of water depressed the f.p. 0·028°; and A. Werner and A. Miolati observed that the electrical conductivity of the soln.

containing a mol of the salt in 1000 litres is practically zero immediately after the salt has dissolved, but as time goes on, hydrolysis occurs, and after a minute, the mol. conductivity, μ, of a soln. with a mol of the salt in 1000 litres, after t minutes, was:

t	1	4	7	10	15	20	60
μ	4·43	8·17	11·95	14·92	20·15	23·88	33·40

E. Petersen found the conductivity of soln. with a mol of the salt in v litres to be:

v	125	250	500	1000	2000	4000
μ at 0° . . .	—	116·5	123·5	128·5	128·8	128·6
μ at 25°. . .	135·2	142·3	155·5	180·0	204·9	242·3

E. Rosenbohm studied the magnetic susceptibility. W. Odling, and W. Lossen observed that the salt is sparingly soluble in cold water but more soluble in hot water; and P. T. Cleve observed that 100 parts of water at 0° dissolve 1 part of the salt, and at 100°, 2·94 to 3·03 parts. C. Gerhardt, and P. T. Cleve found that boiling sulphuric acid, or nitric acid attacks the salt, but boiling aq. ammonia forms a pale yellow soln. of platinic dichlorotetramminochloride, from which alcohol precipitates a white, gum-like mass, soluble in water. A soln. of potassium hydroxide dissolves the salt without the evolution of ammonia, and a dirty yellow precipitate is formed when acids are added to the golden-yellow soln. The chlorine is all precipitated when a soln. of the salt is boiled for a long time with silver nitrate.

P. T. Cleve prepared **platinic *cis*-tetrachlorodiammine,** $[Pt(NH_3)_2Cl_4]$, by treating platinous *cis*-dichlorodiammine with chlorine, or boiling it with nitric acid; and S. M. Jörgensen, by the action of a conc. soln. of ammonium chloride on silver dihydroxychloroplatinate. The orange-yellow powder consists of rhombic or hexagonal plates, or needles. According to P. T. Cleve, the salt loses no weight at 160°, but becomes olive-green; at 210°, it becomes dark green; and at about 240°, slowly decomposes. E. Petersen found that the lowering of the f.p. of a soln. with a mol of the salt in 250 litres is 0·014°. A. Werner and A. Miolati found the electrical conductivity of aq. soln. is nearly zero immediately after the salt has dissolved, but as time goes on, hydrolysis occurs, and the conductivity increases. E. Petersen gave for the conductivities of soln. with a mol of the salt in 125, 250, 500, and 1000 litres at 25°, respectively, 16·9, 20·6, 24·0, and 27·3; and for a soln. of a mol of the salt in 1000 litres:

Age of solution .	0	5	15	30	60 minutes
Mol. conductivity .	25·6	32·0	39·6	53·3	79·2

The nature of the salt was studied by A. Werner and C. H. Herty, and A. Miolati. P. T. Cleve said that 100 parts of water dissolve 0·333 part of salt at 0°, and 1·54 parts at 100°. The salt is not decomposed by conc. sulphuric acid; sulphur dioxide in the boiling aq. soln. forms platinous *cis*-hydrosulphitochlorodiammine, and alkali-lye forms a pale yellow soln. without the evolution of much ammonia.

P. T. Cleve reported **platinic tetrachlorotetrammine,** $Pt(NH_3)_4Cl_4.H_2O$, to be obtained by heating platinic dihydroxytetrammine, $Pt_2(NH_3)_4(OH)_2.H_2O$, with aqua regia. The yellow, amorphous powder is dried at 100°. B. E. Dixon prepared **silver chlorodiamidotriamminochloride,** $[Ag_3\{Pt(NH_3)_3(NH_2)_2Cl\}_2]Cl_5$; and **silver platinic hydroxytriamidodiamminochloride,** $[Ag_2\{Pt(NH_3)_2(NH_2)_3(OH)\}]Cl_2$.

P. T. Cleve prepared **platinic dihydroxydichlorobisamidohexamminochloride,**

$$\left[\begin{matrix}HO\\(NH_3)_3\end{matrix}\!>\!Pt\!<\!\begin{matrix}NH_2\\NH_2\end{matrix}\!>\!Pt\!<\!\begin{matrix}OH\\(NH_3)_3\end{matrix}\right]Cl_4$$

by the action of hydrochloric acid on the nitrate of the series, and drying the product over sulphuric acid, or at 100°. The snow-white, acicular crystals are sparingly

soluble in water; and silver nitrate precipitates all the chlorine from the salt in aq. soln.

Platinic chloride forms a number of complex salts with the alkyl and other amines, sulphines, selenines, phosphines, etc. S. M. Jörgensen [3] prepared **platinic dichloroquatermethylaminechloride**, $[Pt(CH_3NH_2)_4Cl_2]Cl_2$; I. I. Tscherniaeff, **platinic dichloroethylenediaminopyridinoamminochloride**, $[Pt(NH_3)$ en py $Cl_2]Cl_2$; **platinic dichlorethylenediaminodiamminochloride**, $[Pt(NH_3)_2$ en $Cl_2]Cl_2$; **platinic trichloroethylenediaminoamminochloride**, $[Pt(NH_3)$ en $Cl_3]Cl$; **platinic trichloropyridinoethylenediaminochloride**, [Pt en py $Cl_3]Cl$; **platinic trichloropyridinoethylenediaminochloride**, $[Pt(NH_3)$ en $Cl_3]Cl$; **platinic trichloropyridinoethylenediaminochloride**, [Pt en py $Cl_3]Cl.2H_2O$; **platinic trichloropyridinoethylenediaminochloride**, [Pt en py $Cl_3]Cl$; **platinic dichloronitritopyridinoethylenediaminochloride**, [Pt en py $(NO_2)Cl]Cl$; **platinic chlorodinitritopyridinoethylenediaminochloride**, [Pt en py $(NO_2)_2Cl]$ $Cl.2H_2O$; **platinic chlorodinitritopyridinoethylenediaminohydroxide**, [Pt en py $(NO_2)_2Cl]OH$; **platinic chloroamidonitritopyridinoethylenediaminochloride**, [Pt en py $(NH_2)(NO_2)Cl]Cl.2H_2O$; **platinic ehloronitritopyridinoethylenediaminoammonochloride**, $[Pt(NH_3)$ en py $(NO_2)Cl]Cl_2$; **platinic chloronitritoethylenediaminodiamminochloride**, $[Pt(NH_3)_2en(NO_2)Cl]Cl_2$, and **platinic dichloroethylenediaminodiamminochloride**, $[Pt(NH_3)_2$ en $Cl_2]Cl_2$, and its isomeride; **platinic dichloronitritopyridinoethylenediaminochloride**, [Pt en py $(NO_2)Cl_2]Cl$, and its isomerides; **platinic dichloronitritopyridinoethylenediaminohydroxide**, [Pt en py $(NO_2)Cl_2]OH$, and its isomerides; **platinic dichloronitritoethylenediaminoamminochloride**, $[Pt(NH_3)en(NO_2)Cl_2]Cl$, and its isomerides; C. A. Wurtz, T. Anderson, E. Duvillier and A. Buisine, F. W. O. de Coninck, A. Ries, P. Groth, O. Luedecke, E. von Meyer, A. W. Hofmann, L. Berend and C. Stoehr, C. M. Wetherill, O. Mendius, and E. Schmidt described **platinic bismethylaminehydrochloride**, $2(CH_3)NH_2.HCl.PtCl_4$; E. Duvillier and A. Buisine, V. Meyer and M. Lecco, C. Ciamician and P. Silber, J. Bertheaume, W. H. Bresler, A. Ries, J. A. le Bel, T. H. Hjortdahl, O. Luedecke, H. Töpsöe, and P. Groth, **platinic bisdimethylaminehydrochloride**, $2(CH_3)_2NH.HCl.PtCl_4$, or $2(CH_3)_2H_2NCl.PtCl_4$; E. Duvillier and A. Buisine, L. J. Eisenberg, L. Knorr, R. Willstätter, A. Ladenburg, A. W. Hofmann, O. Luedecke, J. Schabus, A. Ries, J. Bertheaume, and T. Langeli, **platinic bistrimethylaminehydrochloride**, $2(CH_3)_3N.HCl.PtCl_4$; and A. W. Hofmann, H. Töpsöe, A. Ries, E. Duvillier and A. Buisine, E. Duvillier, O. Luedecke, E. Schmidt and L. Krauss, and O. Klein, **platinic bistetramethylammonium-ehloride**, $2(CH_3)_4NCl.PtCl_4$. H. Wolffram prepared **platinic dichloroquaterethylamine-chloride**, $[Pt(C_2H_5NH_2)_4Cl_2]Cl_2$; and A. Cossa, **platinic dichloroquaterethylaminechloroplatinite**, $[Pt(C_2H_5NH_2)_4Cl_2]PtCl_4$; P. C. Ray and co-workers, **platinic bisethylaminochloride**, $PtCl_4(C_2H_5NH_2)_2$; C. A. Wurtz, J. Tafel, F. W. Clarke, F. L. Sonnenschein, E. Diepolder, J. Schabus, A. Ries, A. W. Hofmann, A. des Cloizeaux, P. Groth, and H. Töpsöe, **platinic bisethylaminchydrochloride**, $2(C_2H_5)NH_2.HCl.PtCl_4$; A. W. Hofmann, E. Duvillier and A. Buisine, H. Müller, J. Schabus, A. Ries, and H. Töpsöe, **platinic bisdiethylaminehydrochloride**, $2(C_2H_5)_2NH.HCl.PtCl_4$; F. L. Sonnenschein, A. W. Hofmann, E. Duvillier and A. Buisine, A. Ries, and H. Malbot, **platinic bistriethylaminehydrochloride**, $2(C_2H_5)_3N.HCl.PtCl_4$; H. Reihlen and E. Flohr, **platinic tetraethylamine chloride**, $[Pt''ae_4]Cl_2.[Pt''''ae_4Cl_2].4H_2O$; W. Lossen, P. Groth, A. Ries, J. Schabus, A. W. Hofmann, H. Malbot, E. Duvillier and A. Buisine, C. Weltzien, F. L. Sonnenschein, O. Klein, and J. A. le Bel, **platinic bistetraethylammoniumchloride**, $2(C_2H_5)_4NCl.PtCl_4$.

J. A. le Bel, and P. Groth described a complex salt of **platinic methylethylaminehydrochloride**, $(CH_3)(C_2H_5)NH.HCl.PtCl_4$; Z. H. Skraup and D. Wiegmann, J. A. le Bel, and K. Lippitsch, **platinic bismethylethylaminehydrochloride**, $2(CH_3)(C_2H_5)NH.HCl.PtCl_4$; J. A. le Bel, and A. Ries, **platinic bisdimethylethylaminehydrochloride**, $2(CH_3)_2(C_2H_5)N.HCl.PtCl_4$; V. Meyer and M. Lecco, T. H. Hjortdahl, P. Groth, A. Ries, and H. Topsöe, **platinic bismethyldiethylaminehydrochloride**, $2(CH_3)(C_2H_5)_2N.HCl.PtCl_4$; O. Klein, A. Ries, and H. Töpsöe, **platinic bistrimethylethylammonium chloride**, $2(CH_3)_3(C_2H_5)NCl.PtCl_4$; V. Meyer and M. Lecco, A. Ries, and H. Töpsöe, **platinic bisdimethyldiethylammoniumchloride**, $2(CH_3)_2(C_2H_5)_2NCl.PtCl_4$; A. W Hofmann, A. Ries, P. Groth, O. Klein, J. A. le Bel, and H. Töpsöe, **platinic bismethyltriethylammonium-chloride**, $2(CH_3)(C_2H_5)_3NCl.PtCl_4$; A. Ries, **platinic tetramethylammoniumtrimethylethylammoniumchloride**, $(CH_3)_4NCl.(CH_3)_3(C_2H_5)NCl.PtCl_4$; A. Ries, **platinic tetramethylammoniumtrimethylethylammoniumchloride**, $(CH_3)_4NCl.(CH_3)_3(C_2H_5)NCl.PtCl_4$; and A. Ries, **platinic trimethylethylammoniumdimethylethylammoniumchloride**, $(CH_3)_3(C_2H_5)NCl.(CH_3)_2(C_2H_5)_2NCl.PtCl_4$.

T. Anderson, Z. H. Skraup and D. Wiegmann, T. H. Hjortdahl, A. W. Hofmann, K. Lippitsch, H. Töpsöe, A. Ries, O. Mendius, and P. Groth, **platinic bis-*n*-propylaminehydrochloride**, $2(C_3H_7)NH_2HCl.PtCl_4$; A. Siersch, J. Tafel, T. H. Hjortdahl, A. Ries, H. Steinmetz, A. W. Hofmann, and E. Duvillier and A. Buisine, **platinic bis-i-propylaminehydrochloride**, $2(C_3H_7)NH_2.HCl.PtCl_4$; J. A. le Bel, A. Ries, and P. Groth, **platinic bis-n-dipropylaminehydrochloride**, $2(C_3H_7)_2NH.HCl.PtCl_4$; A. Siersch, A. Ries, and J. A. le Bel, **platinic bis-i-dipropylaminehydrochloride**, $2(C_3H_7)_2NH.HCl.PtCl_4$; A. Ries, P. Groth, and J. A. le Bel, **platinic bis-i-propyl-n-propylaminehydrochloride**, $2(C_3H_7)(C_3H_7)NH.HCl.PtCl_4$; H. Malbot, A. Ries, J. A. le Bel, and P. Groth, **platinic bistripropylaminehydrochloride**, $2(C_3H_7)_3N.HCl.$

$PtCl_4$; A. Ries, and P. Groth, **platinic tetrapropylammoniumchloride**, $2(C_3H_7)_4NCl.PtCl_4$; J. A. lo Bel, and P. Groth, **platinic dimethylaminedipropylaminehydrochloride**, $(CH_3)_2NH.HCl.(C_3H_7)_2NH.HCl.PtCl_4$; R. Störmer and V. von Lepel, J. A. le Bel, A. Ries, and P. Groth, **platinic bismethyl-n-propylaminehydrochloride**, $2(CH_3)(C_3H_7)NH.HCl.PtCl_4$; J. A. le Bel, A. Ries, and P. Groth, **platinic bismethyl-i-propylaminehydrochloride**, $2(CH_3)(C_3H_7)NH.HCl.PtCl_4$; J. A. lo Bel, and A. Ries, **platinic dimethylaminedimethylpropylaminehydrochloride**, $(CH_3)_2NH.HCl.(CH_3)_2(C_3H_7)N.HCl.PtCl_4$; J. A. lo Bel, M. Passon, and A. Ries, **platinic bismethyl-n-dipropylaminehydrochloride**, $2(CH_3)(C_3H_7)_2N.HCl.PtCl_4$; J. A. le Bel, A. Ries, and P. Groth, **platinic bismethyl-i-dipropylaminehydrochloride**, $2(CH_3)(C_3H_7)_2N.HCl.PtCl_4$; T. Langeli, A. Ries, and J. A. le Bel, **platinic bistrimethyl-n-propylammoniumchloride**, $2(CH_3)_3(C_3H_7)NCl.PtCl_4$; H. and A. Malbot, J. A. le Bel, and A. Ries, **platinic bistrimethyl-i-dipropylammoniumchloride**, $2(CH_3)_3(C_3H_7)NCl.PtCl_4$; A. Ries, and J. A. le Bel, **platinic bisdimethyldipropylammoniumchloride**, $2(CH_3)_2(C_3H_7)_2NCl.PtCl_4$; A. Ries, and P. Groth, **platinic bismethyltripropylammoniumchloride**, $2(CH_3)(C_3H_7)_3NCl.PtCl_4$, and its five modifications; E. Comanducci and M. Arena, P. Groth, A. Ries, and J. A. le Bel, **platinic bisethyl-n-propylaminehydrochloride**, $2(C_2H_5)(C_3H_7)NH.HCl.PtCl_4$; A. Ries, A. Schuftan; and J. A. lo Bel, **platinic bisethyl-i-propylaminehydrochloride**, $2(C_2H_5)(C_3H_7)NH.HCl.PtCl_4$, A. Rios, and P. Groth, **platinic bisdiethylpropylaminehydrochloride**, $2(C_2H_5)_2(C_3H_7)N.HCl.PtCl_4$; J. A. le Bel, E. Comanducci and M. Arena, M. Passon, A. Ries, and P. Groth, **platinic bisethyldipropylaminehydrochloride**, $2(C_2H_5)(C_3H_7)_2N.HCl.PtCl_4$; O. Mendius, J. A. lo Bel, and A. Ries, **platinic bistriethylpropylammoniumchloride**, $2(C_2H_5)_3(C_3H_7)NCl.PtCl_4$; A. Rios, and J. A. le Bel, **platinic bisdiethyldipropylammoniumchloride**, $2(C_2H_5)_2(C_3H_7)_2NCl.PtCl_4$; J. A. le Bel, A. Ries, and P. Groth, **platinic bisethyltripropylammoniumchloride**, $2(C_2H_5)(C_3H_7)_3NCl.PtCl_4$; A. Ries, J. A. lo Bel, and P. Groth, **platinic bismethylethylpropylaminehydrochloride**, $2(CH_3)(C_2H_5)(C_3H_7)N.HCl.PtCl_4$; J. A. lo Bel, and P. Groth, **platinic methylethylaminedipropylaminehydrochloride**, $(CH_3)(C_2H_5)NH.HCl.(C_3H_7)_2NH.HCl.PtCl_4$; A. Ries, and J. A. lo Bol, **platinic bisdimethylethylpropylammoniumchloride**, $2(CH_3)_2(C_2H_5)(C_3H_7)NCl.PtCl_4$; A. Rios, **platinic bismethyldiethylpropylammoniumchloride**, $2(CH_3)(C_2H_5)_2(C_3H_7)NCl.PtCl_4$; and A. Rios, **platinic bismethylethyldipropylammoniumchloride**, $2(CH_3)(C_2H_5)(C_3H_7)_2NCl.PtCl_4$. F. G. Mann obtained a series of derivatives of **platinic tetrachlorotriaminopropanes**, $[Pt(NH_2.CH_2.CH(NH_2)CH_2(NH_2)Cl_4]$.

A. Lieben and A. Rossi, E. Linnemann and V. Von Zotta, A. Ries, and P. Groth described **platinic bis-n-butylaminehydrochloride**, $2(C_4H_9)NH_2.HCl.PtCl_4$; E. Duvillier and A. Buisine, E. Linnemann, P. Groth, A. Ries, **platinic bis-i-butylaminehydrochloride**, $2(C_4H_9)NH_2.HCl.PtCl_4$; E. Linnemann, A. Ries, B. Braumer, and M. Freund and F. Lenze, **platinic bis-tertiary-butylaminehydrochloride**; A. Lieben and A. Rossi, **platinic bis-n-dibutylaminehydrochloride**, $2(C_4H_9)_2NH.HCl.PtCl_4$; H. Malbot, A. Ries, A. Ehrenborg, J. A. le Bel, and P. Groth, **platinic bis-i-dibutylaminehydrochloride**, $2(C_4H_9)_2NH.HCl.PtCl_4$; A. Lieben and A. Rossi, **platinic bis-n-butylaminehydrochloride**, $2(C_4H_9)_3N.HCl.PtCl_4$; P. Groth, A. Ries, and H. Malbot, **platinic bis-i-tributylaminehydrochloride**, $2(C_4H_9)_3N.HCl.PtCl_4$; A. Ries, two modifications of **platinic bis-i-tetrabutylammoniumchloride**, $2(C_4H_9)_4NCl.PtCl_4$; A. P. N. Franchimont and H. van Erp, **platinic bismethyl-n-butylaminehydrochloride**, $2(CH_3)(C_4H_9)NH.HCl.PtCl_4$; R. Störmer and V. von Lepel, **platinic bismethyl-i-butylaminehydrochloride**, $2(CH_3)(C_4H_9)NH.HCl.PtCl_4$; J. A. le Bel, A. Ries, and P. Groth, **platinic bistrimethyl-n-butylammoniumchloride**, $2(CH_3)_3(C_4H_9)NCl.PtCl_4$; J. A. le Bol, and A. Ries, **platinic bistrimethyl-i-butylammoniumchloride**, $2(CH_3)_3(C_4H_9)NCl.PtCl_4$; A. Rios, **platinic methyltri-i-butylammoniumchloride**, $2(CH_3)(C_4H_9)_3NCl.PtCl_4$; P. Groth, A. Rios, and J. A. le Bel, **platinic bisethyl-n-butylaminehydrochloride**, $2(C_2H_5)(C_4H_9)NH.HCl.PtCl_4$; P. Groth, A. Rios, and W. Marckwald and A. von Droste-Huelshoff, **platinic bisethyl-i-butylaminehydrochloride**, $2(C_2H_5)(C_4H_9)NH.HCl.PtCl_4$; J. A. le Bel, **platinic bisethyl-sec-butylaminehydrochloride**; J. A. le Bel, P. Groth, and A. Ries, **platinic bisethyl-i-dibutylaminehydrochloride**, $2(C_2H_5)(C_4H_9)_2N.HCl.PtCl_4$; A. Ries, two modifications of **platinic bistriethyl-n-butylammoniumchloride**, $2(C_2H_5)_3(C_4H_9)NCl.PtCl_4$; A. Ries, three modifications of **platinic bistriethyl-i-butylammoniumchloride**, $2(C_2H_5)_3(C_4H_9)NCl.PtCl_4$; A. Ries, **platinic bisethyltri-i-butylammoniumchloride**, $2(C_2H_5)(C_4H_9)_3NCl.PtCl_4$; W. Marckwald and A. von Droste-Huelshoff, **platinic bismethylethyl-i-butylaminehydrochloride**, $2(CH_3)(C_2H_5)(C_4H_9)N.HCl.PtCl_4$; W. Marckwald, P. Groth, and A. Ries, **platinic bis-n-propyl-i-butylaminehydrochloride**, $2(C_3H_7)(C_4H_9)NH.HCl.PtCl_4$; J. A. le Bel, A. Rios, and P. Groth, **platinic bis-i-propyl-i-butylaminehydrochloride**, $2(C_3H_7)(C_4H_9)NH.HCl.PtCl_4$; A. Ries and P. Groth, two modifications of **platinic bispropyl-i-dibutylaminehydrochloride**, $2(C_3H_7)(C_4H_9)_2N.HCl.PtCl_4$; A. Ries, **platinic bistripropylbutylammoniumchloride**, $2(C_3H_7)_3(C_4H_9)NCl.PtCl_4$; A. Ries, three modifications of **platinic bispropyltri-i-butylammoniumchloride**, $2(C_3H_7)(C_4H_9)_3NCl.PtCl_4$; P. Groth, A. Ries, and J. A. le Bel, **platinic bisethylpropyl-i-butylaminehydrochloride**, $2(C_2H_5)(C_3H_7)(C_4H_9)N.HCl.PtCl_4$; and A. Ries, W. Marckwald and A. von Droste-Heulshoff, and J. A. le Bel, five modifications of **platinic bismethylethylpropyl-i-butylammoniumchloride**, $2(CH_3)(C_2H_5)(C_3H_7)(C_4H_9)NCl.PtCl_4$.

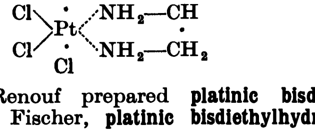
C. A. Wurtz, C. G. Williams, O. Mendius, A. Ries, A. W. Hofmann, and P. Groth described **platinic bisamylaminehydrochloride**, $2(C_5H_{11})NH_2.HCl.PtCl_4$, with *n*-amyl; R. T. Plimpton, A. W. Hofmann, A. Ries, and P. Groth, the active and inactive forms of this salt; J. Tafel, and N. Kursanoff, the compound with secondary amyl; and M. Freund and F. Lenze,

W. Rudneff, A. Ries, and P. Groth, two modifications of the compound with tertiary amyl. A. W. Hofmann, A. Ries, and J. A. lo Bel studied **platinic bisdiamylaminehydrochloride,** $2(C_5H_{11})_2NH.HCl.PtCl_4$, with *n*-amyl; R. T. Plimpton, and R. D. Silva, the compound with inactive iso-amyl, and R. T. Plimpton, the compound with active iso-amyl. A. W. Hofmann studied **platinic bistriamylaminehydrochloride,** $2(C_5H_{11})_3N.HCl.PtCl_4$, with *n*-amyl; R. T. Plimpton, and R. D. Silva, with inactive iso-amyl; and R. T. Plimpton, with active iso-amyl. A. W. Hofmann described **platinic bistetramylammoniumchloride,** $2(C_5H_{11})_4NCl.PtCl_4$; R. Störmer and V. von Lepel, **platinic bismethyl-i-amylaminehydrochloride,** $2(CH_3)(C_5H_{11})NH.HCl.PtCl_4$; J. A. le Bel, and A. Ries, **platinic bistrimethylamylammoniumchloride,** $2(CH_3)_3(C_5H_{11})NCl.PtCl_4$, with active amyl; H. and A. Malbot, O. Schmiedeberg and E. Harnack, J. A. le Bel, A. Ries, and P. Groth, with iso-amyl. J. A. le Bel, A. Ries, and P. Groth studied **platinic bisethyl-i-amylaminehydrochloride,** $2(C_2H_5)(C_5H_{11})NH.HCl.PtCl_4$, with *n*-amyl, and A. Durand, with inactive amyl. A. W. Hofmann described **platinic bisdiethyl-i-amylaminehydrochloride,** $2(C_2H_5)_2(C_5H_{11})N.HCl.PtCl_4$, also **platinic bistriethyl-i-amylammoniumchloride,** $2(C_2H_5)_3(C_5H_{11})NCl.PtCl_4$; and **platinic bismethylethyl-i-amylaminehydrochloride,** $2(CH_3)(C_2H_5)(C_5H_{11})N.HCl.PtCl_4$; S. B. Schryver and J. N. Collie, **platinic bismethyldiethylamylammoniumchloride,** $2(CH_3)(C_2H_5)_2(C_5H_{11})NCl.PtCl_4$; with inactive *n*-amyl, and i-amyl; and J. A. le Bel, and P. Groth, **platinic methylethylpropyl-i-amylammoniumchloride,** $2(CH_3)(C_2H_5)(C_3H_7)(C_5H_{11})NCl.PtCl_4$.

A. Cahours and A. W. Hofmann, H. Malbot, and C. Liebermann and C. Paal described **platinic bisallylaminehydrochloride,** $2(C_3H_5)NH_2.HCl.PtCl_4$; A. Cahours and A. W. Hofmann, and H. Malbot, **platinic bistriallyaminehydrochloride,** $2(C_3H_5)_3N.HCl.PtCl_4$; and **platinic bistetrallylammoniumchloride,** $2(C_2H_5)_4NCl.PtCl_4$; J. Weiss, H. and A. Malbot, and A. Partheil, **platinic bistrimethylallylammoniumchloride,** $2(CH_3)_3(C_3H_5)NCl.PtCl_4$; A. Rinne, and C. Liebermann and C. Paal, **platinic bisethylallylaminehydrochloride,** $2(C_2H_5)(C_3H_5)NH.HCl.PtCl_4$; A. Rinne, and C. Liebermann and C. Paal, **platinic bisdiethylallylaminehydrochloride,** $2(C_2H_5)_2(C_3H_5)N.HCl.PtCl_4$; E. Reboul, **platinic bistriethylallylammoniumchloride,** $2(C_2H_5)_3(C_3H_5)NCl.PtCl_4$; C. Liebermann and C. Paal, **platinic bispropylallyaminehydrochloride,** $2(C_3H_7)(C_3H_5)NH.HCl.PtCl_4$; and P. Groth, and C. Liebermann and C. Paal, **platinic bisdipropylallylaminehydrochloride,** $2(C_3H_7)_2(C_3H_5)N.HCl.PtCl_4$.

N. S. Kurnakoff,[4] and A. Schleicher and co-workers prepared **platinic dichlorobisethylenediaminechloride,** $[Pt\{C_2H_4(NH_2)_2\}_2Cl_2]Cl_2$, and **platinic dichlorobisethylenediaminechlorocuprate,** $[Pt\{C_2H_4(NH_2)_2\}_2Cl_2]CuCl_4$, as well as a complex with platinous bisethylenediaminechlorocuprate—*vide supra*. F. M. Jäger studied the crystals of the first-named salt. W. Schacht, and C. Neuberg prepared **platinic ethylenediaminehydrochloride,** $C_2H_4(NH_2)_2.2HCl.PtCl_4$; J. Lifschitz and E. Rosenbohm studied the optical properties of **platinic trisethylenediaminochloride,** $[Pt\,en_3]Cl_4.2{\cdot}5$ aq. A. P. Smirnoff obtained **platinic trispropylenediaminochloride,** $[Pt(C_3H_6N_2H_4)_3]Cl_4.H_2O$, in its racemic, and dextro-, and lævo-forms. A. Werner, **platinic tetrachloropropylenediamine,** $[Pt\{C_3H_6(NH_2)_2\}Cl_4]$; A. Werner, **platinic dichlorobispropylenediaminechloride,** $[Pt\{C_3H_6(NH_2)_2\}_2Cl_2]Cl_2$; and A. W. Hofmann, **platinic propylenediaminehydrochloride,** $C_3H_6(NH_2)_2.2HCl.PtCl_4$. L. A. Tschugaeff and co-workers prepared **platinic chloroamidotetramminochloride,** $[Pt(NH_3)_4(NH_2)Cl]Cl_2$; and F. G. Mann, **platinic tetrachloro-$\beta\beta'\beta''$-triaminopropanemonohydrochloride,** $[Pt(NH_2.CH_2.CHNH_2.CH_2.NH_2)(HCl)Cl_4].H_2O$; and **platinic tetrachloro-$\beta\beta'\beta''$-triaminopropanemonohydrochloroplatinate,** $[Pt(NH_2.CH_2.CHNH_2.CH_2NH_2)(HCl)]_2PtCl_4.H_2O$; **platinic dichloro-$\beta\beta'\beta''$-triaminotriethylaminochloride,** $[PtN(C_2H_4.NH_2)_3Cl_2]Cl_2$, **platinic dichloro-$\beta\beta'\beta''$-triaminotriethylaminochloroplatinate,** $[PtN(C_2H_4.NH_2)_3Cl_2]PtCl_6.2H_2O$; and also $3PtCl_4.2N(C_2H_4.NH_2)_3.6HCl.10H_2O$.

I. I. Tscherniaeff and A. N. Federova prepared **platinic dichloroethylenediaminodiammine,** $[Pt(NH_3)_2\,en\,Cl_2]Cl_2$; and **platinic nitritochloroethylenediaminodiammine,** $[Pt(NH_3)_2\,en(NO_2)Cl]Cl_2$. The former reacts reversibly with aq. ammonia to form a mixed pentammine, $[Pt(NH_3)_3\,en\,Cl]X_3$, and hexamine, $[Pt(NH_3)_4\,en]X_4$. I. I. Tscherniaeff prepared three of the four possible isomerides of **platinic nitritodichloroethylenediaminomethylaminochloride,** $[Pt\,en\,(CH_3.NH_2)(NO_2)Cl_2]Cl$; and also the optical isomerides of **platinic dinitritochloroethylenediaminomethylaminochloride,** $[Pt\,en\,(CH_3.NH_2)(NO_2)_2Cl]Cl$; and of **platinic dinitritochloroethylenediaminopyridinochloride,** $[Pt\,en\,py\,(NO_2)_2Cl]Cl$; I. I. Shukoff and O. P. Shipulina studied the absorption of **platinic trichloroamminoethylenediaminochloride,** $[Pt(NH_3)\,en\,Cl_3]Cl$, by charcoal. F. G. Mann obtained **platinic tetrachlorodiaminodiethylaminohydrochloride,** $[Cl_4Pt(H_2N.C_2H_4)_2NH.HCl]$, the corresponding **platinic tetrachlorodiaminodiethylaminohydrochloridechloroplatinate,** $[Cl_4Pt(H_2N.C_2H_4)_2NH.HCl]_2PtCl_4.H_2O$, and **platinic trichlorodiaminodiethylamine,** $[PtCl_3.(H_2N.C_2H_4)_2NH]$. F. G. Mann and W. J. Pope prepared optically active **platinum tetrachlorotriaminopropanemonohydrochloride,**



E. Fischer,[5] and E. Renouf prepared **platinic bisdimethylhydrazinehydrochloride,** $2(CH_3)_2N_2H_2.HCl.PtCl_4$; E. Fischer, **platinic bisdiethylhydrazinehydrochloride,** $2(C_2H_5)_2$-

$N_2H_2.HCl.PtCl_4$; and L. A. Tschugaeff and co-workers, **platinic carbylaminohydrazinochloride,** and a chloroplatinate, and L. A. Tschugaeff and A. S. Samsonova also prepared some complexes with hydroxylamine.

A. W. Hofmann,[6] T. Anderson, and E. Lippmann and G. Vortmann prepared **platinic bisanilinehydrochloride,** $2C_6H_5NH_2.HCl.PtCl_4$; O. Widman, **platinic bis-m-toluidinehydrochloride,** $2C_7H_7NH_2.HCl.PtCl_4$; A. W. Hofmann, and J. S. Muspratt and A. W. Hofmann, **platinic bis-p-toluidinehydrochloride,** $2C_7H_7NH_2.HCl.PtCl_4$; O. Pieper, **platinic bisxylidinehydrochloride,** $2C_8H_9NH_2.HCl.PtCl_4$, and isomeric forms were obtained by H. Strassmann, E. Paterno and P. Spica, and E. Bamberger and W. Lodter. H. W. Dudley studied various choline chloroplatinates—*e.g.* **propionylcholinechloroplatinate; n-butyrylcholinechloroplatinate; n-valerylcholinechloroplatinate; n-hexolcholinechloroplatinate;** and **decoylcholinechloroplatinate.**

T. Anderson,[7] C. G. Williams, J. G. Gentele, C. W. Blomstrand, A. Wurtz, C. Liebermann and C. Paal, F. W. O. de Coninck, S. G. Hedin, A. Werner and F. Fassbender, P. C. Ray and co-workers, I. I. Tscherniaeff and A. M. Rubinstein, A. Werner, and S. M. Jörgensen studied the compounds of platinic chloride with pyridine. C. W. Blomstrand, S. M. Jörgensen, T. Anderson, and S. G. Hedin prepared **platinic trans-tetrachlorobispyridine,** $[Pt(C_5H_5N)_2Cl_4]$, and A. Cossa, A. Werner and F. Fassbender, T. Anderson, C. Liebermann and C Paal, L. Balbiano, C. G. Williams, E. Koefoed, and S. G. Hedin, **platinic cis-tetrachlorobispyridine,** $[Pt(C_5H_5N)_2Cl_4]$. S. G. Hedin prepared **platinic dichloroquaterpyridinechloride,** $[Pt(C_5H_5N)_4Cl_2]Cl_2.7H_2O$; A. Cossa, **platinic dichloroquaterpyridinechloroplatinite,** $[Pt(C_5H_5N)_4Cl_2]PtCl_4$; S. G. Hedin, and S. M. Jörgensen, **platinic dichloroquaterpyridinechloroplatinate,** $[Pt(C_5H_5N)_4Cl_2]PtCl_6$; and a complex with platinic pentachloropyridine, $[Pt(C_5H_5N)_4Cl_2][Pt(C_5H_5N)Cl_5]_2.2H_2O$. T Anderson, F. C. Garrett and J. A. Smythe, H. Weidel and K. Hazura, G. Ciamician and P. Silber, W. Königs, A. Ladenburg, M. Delépine and R. Sornet, R. Meyer and A. Tanzen, V. von Lang, and C. G. Williams, **platinic bispyridinehydrochloride,** $2C_5H_5N.HCl.PtCl_4$; T. Anderson, P. T. Cleve, S. M. Jorgenson, C. Liebermann and C. Paal, and A. Werner and F. Fassbender prepared **pyridinium pyridinepentachloroplatinic acid,** $[Pt(C_5H_5N)Cl_5]H(C_5H_5N)$, as well as the salts **lithium pyridinepentachloroplatinate,** $Li[Pt(C_5H_5N)Cl_5].nH_2O$; **sodium pyridinepentachloroplatinate,** $Na[Pt(C_5H_5N)Cl_5].nH_2O$; **potassium pyridinepentachloroplatinate,** $K[Pt(C_5H_5N)Cl_5]$; **rubidium pyridinepentachloroplatinate,** $Rb[Pt(C_5H_5N)Cl_5]$; **cæsium pyridinepentachloroplatinate,** $Cs[Pt(C_5H_5N)Cl_5]$. S. M. Jörgensen prepared **platinic tetrachloropyridineammine,** $[Pt(NH_3)(C_5H_5N)Cl_4]$; S. M. Jörgensen, **platinic hexachlorobispyridinediammine,** $Pt_2(NH_3)_2(C_5H_5N)_2Cl_6$; F. Förster, **platinic dichlorodicarbonylbispyridine,** $Pt_2(CO)_2(C_5H_5N)_2Cl_2$, and the complex salt $Pt_2(CO)_2(C_5H_5N)_2Cl_2[Pt(C_5H_5N)_2Cl_2]_2$. S. I. Khorunschenkoff studied **platinic ethylenediaminobispyridinotetrachloride.**

T. Anderson,[8] T. Wertheim, H. Vohl, C. G. Williams, and A. H. Church and E. Owen studied the compounds of picoline with platinic chloride. J. Dewar, H. Vohl, F. W. O. de Coninck, and W. Ramsay studied **platinic tetrachloropicoline,** $[Pt(C_6H_7N)Cl_4]$; and **platinic tetrachlorobispicoline,** $[Pt(C_6H_7N)_2Cl_4]$; H. Weidel, A. Baeyer, J. N. Collie and W. S. Myers, F. C. Garrett and J. A. Smythe, H. Frese, E. Dürkopf and M. Schlaugk, A. Ladenburg, O. Lange, H. Goldschmidt and E. J. Constam, and C. Stoehr, **platinic bis-α-picolinehydrochloride,** $2C_6H_7N.HCl.PtCl_4$, or $[Pt(C_6H_7N)_2Cl_4]$, as well as the *monohydrate*, and E. Seyfferth reported the *dihydrate*. A. Hesekiel, H. Weidel, A. Baeyer, C. Stoehr, P. Schwarz, A. Ladenburg, A. Ladenburg and J. Sieber, J. Mohler, and F. Bacher prepared **platinic bis-β-picolinehydrochloride,** $2C_6H_7N.HCl.PtCl_4$, or $[Pt(C_6H_7N)_2Cl_4]$; and A. Ladenburg, A. Behrmann and A. W. Hofmann, O. Lange, S. Gabriel and J. Colman, and K. E. Schultze, **platinic bis-γ-picolinehydrochloride,** $2C_6H_7N.HCl.PtCl_4$. T. Anderson, A. Baeyer, and C. Stoehr prepared **picolinium β-picolinepentachloroplatinate,** $[Pt(C_6H_7N)Cl_5]H(C_6H_7N)$.

T. Anderson, A. H. Church and E. Owen, C. G. Williams, and H. Vohl prepared complex salts with lutidine. F. W. O. de Coninck, and C. Stoehr studied **platinic tetrachlorobis-β-lutidine,** $[Pt(C_7H_9N)_2Cl_4]$; F. C. Garrett and J. A. Smythe, A. Ladenburg, A. Ladenburg and F. C. Roth, V. von Lang, A. Hantzsch, **platinic αγ-dimethylpyridinehydrochloride,** $2C_7H_9N.HCl.PtCl_4$; F. C. Garrett and J. A. Smythe, and F. B. Ahrens and R. Gorkow, **platinic α-β′-dimethylpyridinehydrochloride** and its *dihydrate;* M. Conrad and W. Epstein, F. C. Garrett and J. A. Smythe, F. Grünling, A. Ladenburg, C. F. Roth and O. Lange, **platinic αα′-dimethylpyridinehydrochloride;** F. B. Ahrens, **platinic βγ-dimethylpyridinehydrochloride** and its *dihydrate;* and E. Dürkopf, **platinic ββ′-dimethylpyridinehydrochloride.** A. Ladenburg, and C. Stoehr prepared **platinic α-ethylpyridinehydrochloride;** H. Weidel and K. Hazura, A. Ladenburg, C. Stoehr, L. Berend and C. Stoehr, T. Anderson, C. G. Williams, and F. W. O. de Coninck, **platinic β-ethylpyridinehydrochloride;** A. Ladenburg, and J. Ferns and A. Lapworth, **platinic γ-ethylpyridinehydrochloride.** C. Stoehr prepared **lutidinium lutidinepentachloroplatinate,** $[Pt(C_7H_9N)Cl_5]H(C_7H_9N)$.

T. Anderson, F. B. Ahrens, and A. H. Church and E. Owen studied the compounds of collidine with platinic chloride. A. Calm and K. von Buchka, and F. W. O. de Coninck prepared **platinic tetrachlorobiscollidine,** $[Pt(C_8H_{11}N)_2Cl_4]$; I. Guareschi, **platinic bis-αβγ-trimethylpyridinehydrochloride,** $2C_8H_{11}N.HCl.PtCl_4$; F. B. Ahrens, **platinic bis-αγβ′-trimethylpyridinehydrochloride;** A. Hantzsch, E. Dürkopf, F. C. Garrett and J. A. Smythe, P. Riehm, and J. N. Collie, **platinic bis-αγα′-trimethylpyridinehydrochloride;** A. Richard,

F. W. O. de Coninck, H. Weidel and B. Pick, K. E. Schultze, and A. Ladenburg, **platinic bis-α-methyl-γ-ethylpyridinehydrochloride**; H. Vohl, A. Baeyer, A. Hosekiel, and F. Auerbach, **platinic bis-α-methyl-β′-ethylpyridinehydrochloride**; K. E. Schultz and A. Ladenburg, **platinic bis-α-methyl-α′-ethylpyridinehydrochloride,** A. Calm and K. von Buchka, and F. W. O. de Coninck, **platinic bis-β-methyl-γ-ethylpyridinehydrochloride**; A. Ladenburg, E. Lellmann and W. O. Müller, and A. W. Hofmann, **platinic bis-α-propylpyridinehydrochloride**; A. Ladenburg, and W. Königs and G. Happe, **platinic bis-γ′-isopropylpyridinehydrochloride**; and A. Ladenburg, **platinic bis-γ-isopropylpyridinehydrochloride.** A. Calm and K. von Buchka, and F. W. O. de Coninck prepared **collidinum collidinepentachloroplatinate,** $[Pt(C_8H_{11}N)Cl_5]H(C_8H_{11}N)$.

O. Hesse obtained **quinine chloroplatinate,** $(C_{20}H_{25}N_2O_2)_2PtCl_8.3H_2O$; **isoquinine chloroplatinate,** $(C_{20}H_{25}N_2O_2)_2PtCl_6.3H_2O$; **cinchonidine chloroplatinate,** $(C_{19}H_{23}N_2O)_2PtCl_6.2H_2O$; **iso-cinchonidine chloroplatinate,** $(C_{19}H_{23}N_2O)_2PtCl_6.2H_2O$; and **quinamine chloroplatinate,** $(C_{19}H_{25}N_2O_2)_2PtCl_6.2H_2O$.

O. Wallach and F. Lehmann,[9] E. Seyfferth, A. Ladenburg, T. Hjortdahl, V. von Zepharovich, and W. Königs prepared **platinic bispiperidinehydrochloride,** $2C_5H_{11}N.HCl.PtCl_4$, and a complex with alcohol of crystallization; A. Werner and F. Fassbender, **platinic trans-tetrachloropiperidinepyridine,** $[Pt(C_5H_5N)(C_5H_{11}N)Cl_4]$; F. W. O. de Coninck, **platinic tetrachlorobisquinoline,** $[Pt(C_9H_7N)_2Cl_4]$; A. Baeyer, H. Weidel and K. Hazura, E. Lellmann and H. Abt, O. Eckstein, Z. H. Skraup, C. G. Williams, S. Hoogewerf and W. A. van Dorp, G. Goldschmiedt and M. von Schmidt, and F. W. O. de Coninck, **platinic bisquinolinehydrochloride,** $2C_9H_7N.HCl.PtCl_4$, and A. Baeyer described the *monohydrate*, and M. Kretschy, O. Eckstein, Z. H. Skraup, and S. Hoogewerf and W. A. van Dorp, the *dihydrate*. S. Hoogewerf and W. A. van Dorp, and A. Pictet and S. Popovici described **platinic bis-iso-quinolinehydrochloride,** $2C_9H_7N.HCl.PtCl_4$, and its dihydrate; and W. Heintz, **platinic biscarbamidehydrochloride,** $2CO(NH_2)_2.HCl.PtCl_4$, and its *dihydrate*.

F. W. O. de Coninck [10] described **platinic tetrachlorobistetrahydroquinoline,** $[Pt(C_9H_{11}N)_2Cl_4]$; W. Henke, **platinic tetrachlorobispropionitrile,** $[Pt(C_2H_5CN)_2Cl_4]$; W. Henke, and L. Ramberg, **platinic tetrachlorobisbenzonitrile,** $[Pt(C_5H_5CN)_2Cl_4]$; C. Stoehr and M. Wagner, **platinic tetrachloro-ββ-dimethyldipyridine,** $[Pt(C_{12}H_{12}N_2)Cl_4]$; J. Schlenker, **platinic tetrachlorobis-4, 5-dimethylpyrimidine,** $[Pt(C_6N_2H_8)_2Cl_4]$; A. Byk, **platinic tetrachlorobis-4, 5-methylethylpyrimidine,** $[Pt(C_7N_2H_{10})_2Cl_4]$; and E. Hardy and O. Calmels, **platinic tetraehlorojaborine,** $[Pt(C_{22}H_{32}N_4O_4)Cl_4]$; **platinic tetrachlorobisjaborine,** $[Pt(C_{19}H_{25}N_4O_4)_2Cl_4]$; E. H. Keiser, and W. J. Sell and F. W. Dootson prepared **platinic tetrachlorobistrichloropyridine,** $[Pt(C_5H_2Cl_3N)_2Cl_4]$. R. Ziegelbauer, **platinic tetrachloro-o-phenylenebiguanidine,** $[Pt(C_8H_9N_5)Cl_4]$, and the *dihydrate*; E. Hardy and G. Calmels, **platinic tetrachloropilocarpidine,** $[Pt(C_{10}H_{14}N_2O_2)Cl_4]$; and F. W. Pinkard and co-workers, complexes with glycine.

L. Balbiano [11] described some complexes with pyrazol, thus, **platinic tetrachlorobispyrazol,** $[Pt(C_3H_4N_2)_2Cl_4]$; **platinic tetrachlorobis-3, 5-methylpyrazol,** $[Pt(C_4H_5N_2)_2Cl_4]$; **platinic tetrachlorobis-3, 5-methylchloropyrazol,** $[Pt(C_4H_5N_2Cl)_2Cl_4]$; **platinic tetrachlorobis-3, 5-dimethylpyrazol,** $[Pt(C_5H_8N_2)_2Cl_4]$; **platinic tetrachlorobis-3, 5-dimethyltetrachloropyrazol,** $[Pt(C_5H_4N_2Cl_4)_2Cl_4]$; **platinic tetrachlorobis-p-tolylpyrazol,** $[Pt(C_{10}H_{10}N_2)_2Cl_4]$; **platinic dichlorobispyrazol,** $[Pt(C_3H_8N_2)_2Cl_2]$; **platinic dichlorobis-3, 5-methylpyrazol,** $[Pt(C_4H_5N_2)_2Cl_2]$; **platinic dichlorobis-1-ethyl-3, 5-dimethylpyrazol,** $[Pt(C_7H_{11}N_2)_2Cl_2]$; **platinic dichlorobis-1-phenylpyrazol,** $[Pt(C_9H_7N_2)_2Cl_2]$; **platinic dichlorobis-1-phenyltetrachloropyrazol,** $[Pt(C_9H_3N_2Cl_4)_2Cl_2]$; **platinic dichlorobis-o-tolypyrazol,** $[Pt(C_{10}H_9N_2)_2Cl_2]$; **platinic dichloro-p-tolylpyrazol,** $[Pt(C_{10}H_9N_2)_2Cl_2]$; A. Andreocci, and L. Balbiano, **platinic dichlorobis-1-phenyl-3-methylpyrazol,** $[Pt(C_{10}H_9N_2)_2Cl_2]$; L. Balbiano, and L. Balbiano and G. Marchetti, **platinic dichlorobis-1-phenyl-4-methylpyrazol,** $[Pt(C_{10}H_9N_2)_2Cl_2]$; L. Balbiano, **platinic dichlorobis-1-phenyl-3, 5-dimethylpyrazol,** $[Pt(C_{11}H_{11}N_2)_2Cl_2]$; **platinic dichlorobisphenylmethylethylpyrazol,** $[Pt(C_{12}H_{13}N_2)_2Cl_2]$; **platinic dichlorobis-1-phenylmethylethyltrichloropyrazol,** $[Pt(C_{12}H_{10}N_2Cl_3)_2Cl_2]$; and G. Ortoleva, **platinic dichlorobispyridinephenylpyrazol,** $[Pt(C_{12}H_7N_3)_2Cl_2]$.

L. Balbiano [12] described **platinic tetrachlorobisglyoxal,** $[Pt(C_8H_4N_2)_2Cl_4]$; C. Stoehr, **platinic tetrachlorobispyrazine,** $[Pt(C_5H_4N_2)_2Cl_4]$; C. Stoehr, **platinic tetrachlorobis-2, 5-dimethylpyrazine,** $[Pt(C_6H_8N_2)_2Cl_4]$; C. Stoehr and M. Wagner, **platinic tetrachlorobis-2, 5-dimethyl-3-ethylpyrazine,** $[Pt(C_8H_{12}N_2)_2Cl_4]$; and O. Poppenberg, **platinic tetrachlorocinnamylpyridazine,** $[Pt(C_{12}H_{10}N_2)_2Cl_4]$; C. Stoehr, **pyrazinium pyrazinepentachloroplatinate,** $[Pt(C_4H_4N_2)Cl_5]H(C_4H_4N_2)$; **dimethylpyrazinium 2, 5-dimethylpyrazinepentachloroplatinate,** $[Pt(C_6H_8N_2)Cl_5]H(C_6H_8N_2)$; P. Brandes and C. Stoehr, **trimethylpyrazinium 2, 3, 6-trimethylpyrazinepentachloroplatinate,** $[Pt(C_7H_{10}N_2)Cl_5]H(C_7H_{10}N_2)$; C. Stoehr, **2, 5-dimethyl-3-ethylpyrazinepentachloroplatinic acid,** $[Pt(C_8H_{12}N_2)Cl_5]H$; G. T. Morgan and F. H. Burstall, complexes with dipyridyl.

G. Pellizzari [13] described **platinic tetrachlorobis-1, 3, 4-triazol,** $[Pt(C_2H_3N_3)_2Cl_4]$; A. Andreocci, and G. Pellizzari, **platinic tetrachlorobis-1-phenyl-1, 3-triazol,** $[Pt(C_8H_7N_3)_2Cl_4]$; G. Pellizzari and C. Massa, **platinic tetrachlorobis-1-phenyl-2, 3-triazol,** $[Pt(C_8H_7N_3)_2Cl_4]$; G. Pellizzari and C. Massa, **platinic tetrachlorobis-o-tolyl-1, 3-triazol,** $[Pt(C_9H_9N_3)_2Cl_4]$; and **platinic tetrachlorobis-p-tolyl-1, 3-triazol,** $[Pt(C_9H_9N_3)_2Cl_4]$; G. Pellizzari and M. Bruzzo, **platinic tetrachlorobis-o-tolyl-2, 3-triazol,** $[Pt(C_9H_9N_3)_2Cl_4]$; and **platinic tetra-**

chlorobis-p-tolyl-2, 3-triazol, $[Pt(C_9H_9N_3)_2Cl_4]$; G. Pellizzari and C. Massa, **platinic tetrachlorobis-α-naphthyl-1, 3-triazol,** $[Pt(C_{12}H_9N_3)_2Cl_4]$; and **platinic tetrachlorobis-β-naphthyl-1, 3-triazol** ; G. Pellizzari and M. Bruzzo, **platinic tetrachlorobis-α-naphthyl-2, 3-triazol,** $[Pt(C_{12}H_9N_3)_2Cl_4]$; and **platinic tetrachlorobis-β-naphthyl-2, 3-triazol-1** ; A. Andreocci, **platinic tetrachlorobis-1-phenyl-3-methyl-1, 3-triazol,** $[Pt(C_9H_9N_3)_2Cl_4]$; and G. Pellizzari and A. Alciatore, **platinic tetrachlorobis-o-tolyl-2, 5-dimethyl-2, 3-triazol,** $[Pt(C_{11}H_{13}N_3)_2Cl_4]$; and **platinic tetrachlorobis-o-tolyl-2, 5-dimethyl-2, 3-triazol.** A. Andreocci, **platinic dichlorobis-1-phenyl-3-methyl-1, 3-triazol,** $[Pt(C_9H_8N_3)_2Cl_2]$; and **platinic dichlorobis-1-phenyl-3-methyl-1, 3-triazolone,** $[Pt(C_9H_8ON)_2Cl_2]$. G. Cuneo obtained **platinic tetrachlorobis-1-phenyl-3-imidotriazoline,** $[Pt(C_8H_8N_4)_2Cl_4]$; and **platinic tetrachlorobis-p-tolyl-3-imidotriazoline,** $[Pt(C_9H_{10}N_4)_2Cl_4]$. S. Ruhemann and H. E. Stapleton, S. Ruhemann and R. W. Merriman, O. Hantzsch and O. Silberrad, and G. Pellizzari prepared **platinic tetrachlorobistetrazoline,** $[Pt(C_2H_4N_4)_2Cl_4]$; and S. Ruhemann and R. W. Merriman, and G. Pellizzari, **platinic tetrachlorobisdimethyltriazoline,** $[Pt(C_4H_8N_4)_2Cl_4]$. L. Claisen prepared **platinic tetrachlorobis-α-methylisoxazol,** $[Pt(C_4H_5NO)_2Cl_4]$; and E. Hardy and G. Calmels, **platinic tetrachlorobis-β-hydroxyethylpyridine,** $[Pt(C_7H_9NO)_2Cl_4]$.

P. T. Clove [14] described **platinic hydroxyacetatotetramminochloride,** $[Pt(NH_3)_4(OH)(C_2H_3O_2)]Cl_2$, and **platinic hydroxyacetatotetramminochloroplatinite,** $[Pt(NH_3)_4(OH)(C_2H_3O_2)]PtCl_4.H_2O$; G. Wallin, **platinic tetrachlorobisamidoacetate,** $[Pt(NH_2.CH_2.COOH)_2Cl_4]$, and **platinic tetrachlorobisethylamidoacetate,** $[Pt(NH_2.CH_2.COOC_2H_5)_2Cl_4]$; E. Hardy and G. Calmels, **platinic tetrachlorobis-β-pyridine-α-lactate,** $[Pt(C_8H_9NO_3)_2Cl_4]$; E. Hardy and G. Calmels, **platinic tetrachlorojaborinate,** $[Pt(C_{19}H_{25}N_3O_5)Cl_4]$; and **platinic tetrachlorobisjaborinate,** $[Pt(C_{19}H_{25}N_3O_5)_2Cl_4]$; G. Wallin, **platinic dichlorobisglycine,** $[Pt(NH_2.CH_2COO)_2Cl_2]$; B. Unger, **pentachloroguanineplatinic acid,** $[Pt(C_5H_5N_5O)Cl_5]H.2H_2O$; and A. Hantzsch, **platinic dichloroquatermethylpseudolutidostyrilchloride,** $[Pt(C_8H_{11}NO)_4Cl_2]Cl_2$.

M. Lesbre and E. Gardner prepared the **guanidine salts,** $[Pt(CH_5N_3)Cl](OH)_n$, and $[Pt(CH_5N_3)Cl_2]_2$; and the **cyanurtriamide salts,** $[Pt(C_3N_3(NH_2)_3Cl](OH)_n$.

C. Enebuske,[15] A. Loir, P. C. Ray and P. C. Mukherjee, P. C. Ray, and L. Tschugaeff and J. Benewolensky prepared **platinic tetrachlorobisdimethylsulphine,** $[Pt\{(CH_3)_2S\}_2Cl_4]$; G. Carrara, G. L. Laird, A. Cahours, D. Strömholm, and H. Klinger, **platinic bistrimethylsulphoniumchloride,** $2(CH_3)_3SCl.PtCl_4$; C. W. Blomstrand, M. Weibull, F. G. Angell and co-workers, and A. Loir, **platinic tetrachlorobisdiethylsulphine,** $[Pt\{(C_2H_5)_2S\}_2Cl_4]$; A. von Oefele, K. A. Jensen, F. Dehn, P. Groth, H. Klinger and A. Maassen, and G. Carrara, **platinic bistriethylsulphoniumchloride,** $2(C_2H_5)_3SCl.PtCl_4$; D. Strömholm, **platinic tetrachlorobismethylethylsulphine,** $[Pt\{(CH_3)(C_2H_5)S\}_2Cl_4]$; H. Klinger and A. Maassen, G. L. Laird, and G. Carrarra, **platinic bisdimethylethylsulphoniumchloride,** $2(CH_3)_2(C_2H_5)SCl.PtCl_4$; F. Krüger, R. Nasini and A. Scala, D. Strömholm, W. Lossen, and H. Klinger and A. Maassen, **platinic bismethyldiethylsulphoniumchloride,** $2(CH_3)(C_2H_5)_2SCl.PtCl_4$; C. Rudelius, and M. Weibull, **platinic tetrachlorobisdipropylsulphine,** $[Pt\{(C_3H_7)_2S\}_2Cl_4]$; A. Cahours, **platinic bistripropylsulphoniumchloride,** $2(C_3H_7)_3SCl.PtCl_4$; G. Aminoff, P. Groth, and D. Strömholm, **platinic bismethyldi-n-propylsulphoniumchloride,** $2(CH_3)(C_3H_7)_2SCl.PtCl_4$, as well as the corresponding **platinic bismethyldi-i-propylsulphoniumchloride** ; A. Cahours, **platinic bisdiethylpropylsulphoniumchloride,** $2(C_2H_5)_2(C_3H_7)SCl.PtCl_4$; G. Aminoff, and D. Stromholm, **platinic bismethylethyl-n-propylsulphoniumchloride,** $2(CH_3)(C_2H_5)(C_3H_7)SCl.PtCl_4$, and **platinic bismethylethyl-i-propylsulphoniumchloride** ; H. Löndahl, **platinic tetrachlorobisdi-n-butylsulphine,** $[Pt\{(C_4H_9)_2S\}_2Cl_4]$; H. Löndahl, and M. Weibull, **platinic tetrachlorobisdi-i-butylsulphine** ; A. Cahours, **platinic bistributylsulphoniumchloride,** $2(C_4H_9)_3SCl.PtCl_4$; D. Stromholm, **platinic bismethyldi-i-butylsulphoniumchloride,** $2(CH_3)(C_4H_9)_2SCl.PtCl_4$, and its *hydrate*. G. Aminoff, P. Groth, and D. Stromholm, **platinic bismethylethyl-n-butylsulphoniumchloride,** $2(CH_3)(C_2H_5)(C_4H_9)SCl.PtCl_4$, **platinic bismethylethyl-i-butylsulphoniumchloride,** as well as the corresponding compound with secondary butyl ; D. Strömholm, **platinic methyl-n-propyl-i-butylsulphoniumchloride,** $2(CH_3)(C_3H_7)(C_4H_9)SCl.PtCl_4$, and **platinic methyl-i-propyl-i-butylsulphoniumchloride** ; D. Strömholm, **platinic bismethylethylamylsulphoniumchloride,** $2(CH_3)(C_2H_5)(C_5H_{11})SCl.PtCl_4$; H. Löndahl, **platinic tetrachlorodibenzylsulphine,** $[Pt\{(C_6H_5.CH_2)_2S\}_2Cl_4]$; A. Cahours, **platinic bisdimethylbenzylsulphoniumchloride,** $2(CH_3)_2(C_7H_7)SCl.PtCl_4$; D. Strömholm, **platinic bismethylethylbenzylsulphoniumchloride,** $2(CH_3)(C_2H_5)(C_7H_7)SCl.PtCl_4$; D. Strömholm, **platinic bismethyl-i-propylbenzylsulphoniumchloride,** $2(CH_3)(C_3H_7)(C_7H_7)SCl.PtCl_4$; and A. Husemann, and H. Löndahl, **platinic tetrachlorobisethylenesulphine,** $[Pt\{S(C_2H_4)_2S\}Cl_4]$.

G. Prätorius-Seidler prepared **platinic bisthiocarbamidehydrochloride,** $2CS(NH_2)_2.HCl.PtCl_4$; W. Schacht, **platinic tetrachlorobistrimethylenethiocarbamide,** $[Pt\{HS.C:N(CH_3)_3.NH\}_2Cl_4]$; A. W. Hofmann, and W. Schacht, **platinic tetrachlorobisdiethylenethiocarbamide,** $[Pt(S:C.NH:CH_2.CH_2:NH)_2Cl_4]$; and A. W. Hofmann, and A. Girard, **platinic tetrachlorobistrithioformaldehyde,** $[Pt(C_3H_6S_3)_2Cl_4]$.

W. Marckwald, and A. Wohl and W. Marckwald described **platinic tetrachlorobisimidoazolylmercaptan,** $[Pt(HS.C.NH.CH:CH.N:)_2Cl_4]$; W. Marckwald, **platinic tetrachlorobis-μ-imidoazolylmercaptan,** $[Pt(HS.C.NH.CH:CH.N:)_2Cl_4]$; **platinic tetrachlorobis-ν-methylimidoazolyl-μ-mercaptan,** $[Pt\{HS.C.N(CH_3).CH:CH.N:\}_3Cl_4]$; **platinic tetrachlorobis-ν-phenylimidoazolyl-μ-mercaptan,** $[Pt\{HS.C.N(C_6H_5)CH:CH.N:\}_2Cl_4]$; **platinic tetrachlorobis-ν-p-tolyl-**

imidoazolyl-μ-mercaptan, $[Pt\{HS.C.N(C_6H_4.CH_3)CH : CH.N :\}_2Cl_4]$; **platinic tetrachlorobis-ν-m-xylylimidoazolyl-μ-mercaptan,** $[Pt\{HS.C.N.C_6H_3(CH_3)_2.CH : CH.N :\}_2Cl_4]$; and **platinic tetrachlorobis-ν-α-naphthylimidoazolyl-μ-mercaptan,** $[Pt\{HS.C.NC_{10}H_7.CH : CH.N :\}_2Cl_4]$. P. C. Ray and co-workers described **platinum methylmercaptidochloride,** $PtCl(CH_3)_2S_2.H_2O$; **platinum mercaptidochloride,** $PtCl(C_2H_5)_2S_2$, and **platinum mercaptidobromide,** $PtBr(C_2H_5)_2S_2$, in which it is assumed that the platinum is quinquivalent—*vide supra*, the valency of platinum ; and also $Pt_5Cl(R_2S_2)_4$, in which only one platinum atom is quinquivalent.

F. W. Semmler prepared **platinic disulphovinylsulphinevinylchloroplatinate,** $3[Pt\{(C_2H_3)_2S\}S_2].2C_2H_3Cl.PtCl_4$; F. W. Semmler, and T. Wertheim, **platinic disulphoallyl-sulphineallylchloroplatinate,** $3[Pt\{(C_3H_5)_2S\}S_2].2C_3H_5Cl.PtCl_4$; and C. H. Keutgen, **platinic tetrachlorodiallylhexasulphine,** $Pt\{(C_3H_5)_2S_6\}Cl_4]$.

C. L. Jackson [15] described **platinic tetrachlorobisdimethylselenine,** $[Pt\{(CH_3)_2Se\}_2Cl_4]$; C. L. Jackson, **platinic bistrimethylselenoniumchloride,** $2(CH_3)_3SeCl.PtCl_4$; J. Petren, **platinic tetrachlorobisdiethylselenine,** $Pt\{(C_2H_5)_2Se\}_2Cl_4]$; A. F. W. Schimper, and L. von Pieverling, **platinic triethylselenoniumchloride,** $2(C_2H_5)_3SeCl.PtCl_4$; J. Petren, **platinic tetrachlorodiethylseleninediethylsulphine,** $Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}Cl_4]$; J. Petren, **platinic tetrachlorobisdiethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2Cl_4]$; C. L. Jackson, **platinic tetrachlorobisdibenzylselenine,** $[Pt\{(C_6H_5.CH_2)_2Se\}_2Cl_4]$; and **platinic bisdimethylbenzylselenoniumchloride,** $2(CH_3)_2(C_7H_7)SeCl.PtCl_4$. A. Cahours described **platinic bistrimethyltelluroniumchloride,** $2(CH_3)_3TeCl.PtCl_4$.

A. Cahours and A. W. Hofmann [17] described **platinic bistrimethylphosphinehydrochloride,** $2(CH_3)_3P.HCl.PtCl_4$; A. Cahours and A. W. Hofmann, A. Partheil and A. van Haaren, and J. N. Collie, **platinic bistetramethylphosphoniumchloride,** $2(CH_3)_4PCl.PtCl_4$; A. W. Hofmann, **platinic bisethylphosphinehydrochloride,** $2(C_2H_5)PH_2.HCl.PtCl_4$; and **platinic bisdiethylphosphinehydrochloride,** $2(C_2H_5)_2PH.HCl.PtCl_4$; E. Drechsel and E. Finkelstein, and A. Cahours and A. W. Hofmann, **platinic bistriethylphosphinehydrochloride,** $2(C_2H_5)_3P.HCl.PtCl_4$; Q. Sella, A. Cahours and A. W. Hofmann, **platinic bistetraethylphosphoniumchloride,** $2(C_2H_5)_4PCl.PtCl_4$; A. Cahours, **platinic bistrimethylethylphosphoniumchloride,** $2(CH_3)_3(C_2H_5)PCl.PtCl_4$; J. N. Collie, **platinic bisdimethyldiethylphosphoniumchloride,** $2(CH_3)_2(C_2H_5)_2PCl.PtCl_4$; A. W. Hofmann, and A. Cahours and A. W. Hofmann, **platinic bismethyltriethylphosphoniumchloride,** $2(CH_3)(C_2H_5)_3PCl.PtCl_4$; J. N. Collie, **platinic bistriethylpropylphosphoniumchloride,** $2(C_2H_5)_3(C_3H_7)PCl.PtCl_4$; R. H. Pickard and J. Kenyon prepared **trimethyloxyphosphoniumchloroplatinate,** $4(CH_3)_3PO.H_2PtCl_6$; and a similar compound was obtained by J. A. Collie : **triethyloxyphosphoniumchloroplatinate,** $4(C_2H_5)_3PO.H_2PtCl_5$; and **tripropyloxyphosphoniumchloroplatinate,** $6(C_3H_7)_3PO.H_2PtCl_6$; A. Cahours and A. W. Hofmann, **platinic bistrimethylamylphosphoniumchloride,** $2(CH_3)_3(C_5H_{11})PCl.PtCl_4$; J. N. Collie, and A Cahours and A. W. Hofmann, **platinic bistriethylamylphosphoniumchloride,** $2(C_2H_5)_3(C_5H_{11})PCl.PtCl_4$; A. W. Hofmann, **platinic bistriethylallylphosphoniumchloride,** $2(C_2H_5)_3(C_3H_5)PCl.PtCl_4$; and J. N. Collie, **platinic bisethyltribenzylphosphoniumchloride,** $2(C_2H_5)(C_7H_7)_3PCl.PtCl_4$. F. Fleissner, E. A. Letts and J. N. Collie, and R. H. Pickard and J. Kenyon described **platinic trichlorotrisbenzyloxyphosphinechloride,** $[Pt\{(C_7H_7)_3PO\}_3Cl_3]Cl$.

E. Pomey, and A. Rosenheim and W. Löwenstamm described **platinic tetrachlorobistriethylphosphite,** $[Pt\{P(OC_2H_5)_3\}_2Cl_4]$; A. Michaelis, **platinic tetrachlorobis-p-dimethyloxyphosphinebenzoate,** $[Pt\{(CH_3)_2PO(C_6H_4.COOH)\}_2Cl_4]$; E. Pomey, **platinic tetrachlorotriethylphosphite,** $[Pt\{P(OC_2H_5)_3\}Cl_4]$; A. Rosenheim and W. Löwenstamm, and A. Rosenheim and W. Levy, **platinic tetrachlorotriethylphosphate,** $[Pt\{OP(OC_2H_5)_3\}Cl_4]_2$. P. Schützenberger, and P. Schützenberger and C. Fontaine described a number of ill-defined complexes with phosphorus compounds.

W. M. Dehn and B. B. Wilcox [18] described **platinic bisdimethylarsinehydrochloride,** $2(CH_3)_2AsH.HCl.PtCl_4$; E. Amort, A. Partheil and E. Amort, and E. Mannheim, **platinum bistetramethylarsoniumchloride,** $2(CH_3)_4AsCl.PtCl_4$, or $[(CH_3)_3AsCl]_2PtCl_4$; E. Amort, A. Partheil and E. Amort, E. Mannheim, and H. Landolt, **platinic bistetraethylarsoniumchloride,** $2(C_2H_5)_4AsCl.PtCl_4$, or $[(C_2H_5)_4AsCl]_2PtCl_4$; A Cahours, **platinic bisdimethyldiethylarsoniumchloride,** $2(CH_3)_2(C_2H_5)_2AsCl.PtCl_4$; E. Mannheim, E. Amort, and A. Partheil and E. Amort, **platinic bistetra-n-propylarsoniumchloride,** $2(C_3H_7)_4AsCl.PtCl_4$, and **platinic bistetra-i-propylarsoniumchloride,** or $[(C_3H_7)_3AsCl]_2PtCl_4$; E. Mannheim, E. Amort, and A. Partheil and E. Amort, **platinic bistetrabutylarsoniumchloride,** $2(C_4H_9)_4AsCl.PtCl_4$, or $[As(C_4H_9)_3AsCl]_2.PtCl_4$; A. Partheil and E. Amort, A. Gronover, and A. Michaelis and U. Paetow, **platinic bistetrabenzylarsoniumchloride,** $2As(C_7H_7)_4Cl.PtCl_4$, or $[(C_7H_7)_3AsCl]_2PtCl_4.H_2O$; and A. Michaelis and U. Paetow, **platinic bismethyltribenzylarsoniumchloride,** $2(CH_3)(C_7H_7)_3AsCl.PtCl_4$.

H. Landolt described **platinic bistetramethylstiboniumchloride,** $2(CH_3)_4SbCl.PtCl_4$; R. Löwig, **platinic quatertetraethylstiboniumchloride,** $4(C_2H_5)_4SbCl.3PtCl_4$; A. Partheil and E. Mannheim, and G. B. Buckton, **platinic bistetraethylstiboniumchloride,** $2(C_2H_5)_4SbCl.PtCl_4$; A. Partheil and E. Mannheim, **platinic bistetrapropylstiboniumchloride,** $2(C_3H_7)_4SbCl.PtCl_4$; and G. T. Morgan and V. E. Yarsley obtained **platinous trimethylstibinochloroplatinate,** $[Pt\{(CH_3)_3Sb\}_4]PtCl_4$.

Hydrochloroplatinic acid, H_2PtCl_6, as indicated above, furnishes a series of salts, the chloroplatinates, R_2PtCl_6, typified by **ammonium chloroplatinate,** $(NH_4)_2PtCl_6$, which, as shown by E. von Meyer,[19] is not to be regarded as a double salt of ammonium chloride and platinic chloride. J. J. Berzelius, and J. Thomsen said that ammonium chloroplatinate is precipitated as a lemon-yellow, crystalline powder on adding a soln. of an ammonium salt to one of platinic chloride. If the tint is reddish-yellow, ammonium chloroiridate is probably present, and this impurity can be nearly all removed by boiling with nitric acid. J. W. Döbereiner suggested a method of purification by adding an excess of calcium oxide to the hydrochloroplatinic acid, to precipitate iron, copper, palladium, rhodium, and iridium oxides, before treatment with ammonium chloride. K. Seubert prepared the salt of a high degree of purity for at. wt. determinations :

A conc. soln. of ammonium chloride is poured into a dil. soln. of purified hydrochloroplatinic acid. The precipitate is washed by decantation successively with water, alcohol, and water until the filtrate has but a scarcely perceptible acidic reaction. The precipitate is collected on a suction filter, dried in vacuo over sulphuric acid, and then in an air-bath at 100° to 110°. The ammonium chloroplatinate so obtained can be reduced with hydrogen at 180°, washed by decantation with water, and ignited. The resulting spongy platinum is dissolved in dil. aqua regia, and the soln. evaporated many times with conc. hydrochloric acid. The product is dissolved in acidulated water, concentrated by evaporation in a current of chlorine until a drop of the liquid furnishes a crystalline mush when cooled on a glass plate. The crystals are separated from the cold liquid by a suction-filter, and dissolved in acidulated water so that the soln. has about 34·5 grms. of platinum per 1200 c.c. This soln., cooled by ice, is mixed with a soln. of 50 grms. of ammonium chloride in 1200 c.c. of water, and the precipitate washed by decantation with acidulated, ice-cold water, and dried as indicated above. The spongy platinum can also be dissolved in aqua regia, or hydrochloric acid through which a current of chlorine is passing whilst the liquid is heated on a water-bath.

W. Halberstadt obtained the salt for at. wt. determinations as follows :

Platinum was dissolved in aqua regia, and the soln. evaporated repeatedly with conc. hydrochloric acid, and finally the diluted soln. was concentrated in a current of chlorine. Insufficient ammonium chloride was added to precipitate all the platinum, the filtrate was again treated with insufficient ammonium chloride for complete precipitation, and the operation repeated on the filtrate once more. The three precipitates were separately washed, dried, and ignited. Each of the resulting products was boiled with hydrochloric acid, washed with water, calcined and weighed. The platinum was dissolved in aqua regia, etc., as before, and after evaporating the dil. soln. in a current of chlorine, the residue was dissolved in water, and an ice-cold soln. of the calculated quantity of ammonium chloride was added whilst the soln. was being stirred. The precipitate was washed by decantation with water, separated on a suction-filter, and dried in an air-bath at 150°.

S. M. Jörgensen mixed an aq. soln. of a mol of pentahydrated platinic chloride with a mol of ammonia, evaporated the liquid, and extracted the product with cold water to remove soluble impurities. E. H. Archibald purified the platinum in the following manner :

The metal was precipitated from a soln. of the chloride as ammonium chloroplatinate, the precipitate being thoroughly washed and dried and then reduced in a current of pure hydrogen. After removal of ammonium chloride, the platinum-black was boiled with successive portions of concentrated hydrochloric acid to dissolve out traces of iron. The platinum was then redissolved, and the above processes repeated several times. After three operations all indications of iridium had disappeared. To avoid the difficulty of removing the last traces of nitric acid from a soln. prepared by dissolving platinum in aqua regia, the metal was brought into soln. by making it the anode in an electrolytic cell containing hydrochloric or hydrobromic acid. Ammonium or potassium chloroplatinate or bromoplatinate was obtained from a soln. of purified platinum chloride or bromide as indicated above.

Analyses of the salt were made by J. J. Berzelius, K. Seubert, W. Halberstadt, F. Schulze, P. C. Ray and A. C. Ghosh, and S. M. Jörgensen. As shown by J. J. Berzelius, and H. St. C. Deville and J. S. Stas, precipitated ammonium chloroplatinate is a lemon-yellow, crystalline powder ; and when crystallized from its aq. soln., it yields orange-yellow octahedra. J. J. Berzelius added that a reddish-

yellow colour is produced if iridium be present, and, according to T. Wilm, if palladium or rhodium be present. E. Carozzi observed that the yellow octahedral crystals are isomorphous with the corresponding salts of lead, and tin. According to A. Ries, the cubic crystals appear in three forms: (i) Hexakistetrahedral crystals, stable at low temp., and the cleavage is octahedral; (ii) Pseudoctahedral crystals stable up to 0°, and the cleavage is pseudoctahedral; and (iii) Hexakisoctahedral crystals from a little below 0° up to the temp. of decomposition, and the cleavage is octahedral. There is possibly a fourth pseudocubic form stable at very low temp. G. Engel gave a=9·834 A. for the cubic lattice. P. Niggli and W. Nowacki discussed the crystals. M. L. Huggins, G. B. Naess and O. Hassel, and R. W. G. Wyckoff and co-workers studied the lattice structure of methylammonium chloroplatinate. E. Carozzi studied the isomorphism with ammonium chlorostannate. According to C. H. D. Bödeker, the sp. gr. is 2·995 to 3·009; H. Töpsöe gave 3·065; E. Carozzi, 3·009; and E. H. Archibald, 3·034. R. Romanis discussed the mol. vol.

P. Vallet said that decomposition by heat commences at 250° and is complete at 430°, and the reduction by hydrogen commences at 120°, and is complete at 200°. E. H. Archibald observed that the salt is slightly decomposed at 185°. J. J. Berzelius observed that when heated below redness, there is formed a greyish-green powder, probably, ammonium chloroplatinite. S. M. Jörgensen observed that platinous cis- and trans-dichlorodiammine are formed. J. J. Berzelius, and P. C. Ray and A. C. Ghosh found that at a higher temp., the salt is decomposed, without melting, to form platinum, hydrogen chloride, nitrogen, and ammonium chloride, and E. J. Maumené thought that some NH.HCl is produced. W. Knop observed that the compound precipitated from a conc. hydrochloric acid soln., washed and dried at 100°, and rapidly cooled, decrepitates vigorously when heated, owing to the presence of occluded nitrogen which can be liberated by dissolution in soda-lye. J. Thomsen gave for the heat of formation (Pt, $2Cl_2$, $2NH_4Cl$, Aq.) =84·62 Cals. P. Walden found the eq. conductivity, λ, of a soln. of a gram-equivalent in v litres, to be:

v	64	128	256	512	1024
λ	115·5	120·0	124·1	127·1	129·3

Observations were also made by S. Nagami. E. Feytis gave for the magnetic susceptibility, $-0{\cdot}42\times10^{-6}$ mass unit. N. W. Fischer, and W. Crookes observed that 1 part of ammonium chloroplatinate will communicate a yellow tinge to 20,000 parts of **water**, and that 100 parts of cold water dissolve 0·667 part of salt, and with boiling water, 1·25 parts. A. von Mussin-Puschkin measured the solubility of the salt. E. H. Archibald and J. W. Kern found the solubility, S grms. $(NH_4)_2PtCl_6$ in 100 grms. of water, to be:

	0·1°	7·2°	18·0°	25·4°	49·7°	60·2°	80 2°	99 0°
S .	0·2902	0·3652	0·4869	0·5760	1·0131	1·4740	2·1800	3·2515

and at 20°, for soln. with C mol of ammonium chloride per litre,

C	2·000	1·000	0·200	0·100
S	0·0024	0·0028	0·0186	0·0423

E. Ogawa's observations on the mutual solubility of ammonium chloroplatinate and chloroiridate, at 25°, are summarized in Figs. 80 and 81. L. Pigeon noted that when heated 5 hrs. in **chlorine** at 360°, the salt lost 12·23 per cent. in weight; and W. Knop found that when chlorine is passed into water with the salt in suspension, nitrogen is evolved, and hydrochloroplatinic and hydrochloric acids are formed. N. W. Fischer found that the salt is insoluble in cold **hydrochloric acid,** and its soln. in hot hydrochloric acid deposits the salt on cooling. K. Birnbaum studied the action of sulphurous acid. W. Knop observed that the salt is decomposed by hot, conc. **sulphuric acid,** and N. W. Fischer, that its soln. in hot, dil. sulphuric

acid deposits the salt on cooling. P. Schottländer observed that with **sodium thiosulphate,** there is formed a complex between sodium thiosulphate, and platinum sulphite. R. Fresenius found that the salt is very slightly soluble in aq. **ammonia** in the cold, but it readily dissolves in the hot liquid, forming, according to N. W. Fischer, a colourless or pale yellow liquid. The ammoniacal soln. is stable in closed vessels, but when exposed to air, or when evaporated, it deposits a greyish-white precipitate; and a precipitate is also formed when the ammoniacal soln. is

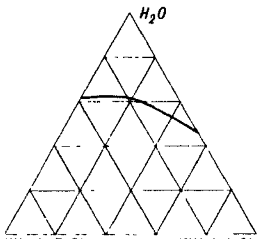


FIG. 80.—The System: $(NH_4)_2PtCl_6$–$(NH_4)_2IrCl_6$–H_2O.

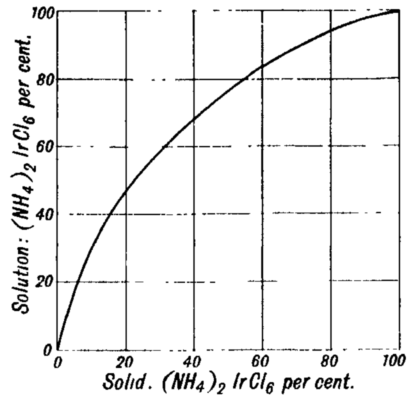


FIG. 81.—The Solubility of Ammonium chloroiridate in the presence of the chloroplatinate.

treated with conc. acids—phosphoric, sulphuric, nitric, or hydrochloric—with alkali carbonates, phosphates, sulphates, and oxalates, and with ferrous sulphate. A. Laurent and C. Gerhardt found that alcohol precipitates from the ammoniacal soln. a white amorphous mass approximately $N_4H_{10}PtCl_2$—but the composition is not constant. J. J. Berzelius, and W. Knop noted that when ammonium chloroplatinate is digested with aq. ammonia, a pale greenish-yellow powder is formed, containing, probably, some $[Pt(NH_3)_4]PtCl_4$. R. Böttger observed that a conc. soln. of **ammonium chloride** precipitates the salt almost completely from its aq. soln., and H. St. C. Deville and J. S. Stas said that the salt is sparingly soluble in a cold, sat. soln. of ammonium chloride, and that the yellow soln. slowly becomes colourless in contact with the chloroplatinate, or when warmed to 100°. N. W. Fischer observed that the salt crystallizes out on cooling a soln. in hot **nitric acid.** I. I. Shukoff and O. P. Schipulina found that the salt decomposes when absorbed on **charcoal.** For the reduction by **carbon monoxide,** *vide supra,* colloidal platinum. The salt is insoluble in **ether,** and in absolute **alcohol.** R. Fresenius studied the solubility in alcohol. J. Dalietos and K. Makris found alcohol vapour is oxidized by sodium but not by potassium chloroplatinate. According to R. Fresenius, at 15° to 20°, 1 part of the salt dissolves in 26,535 parts of 97·5 per cent. alcohol, in 1·476 parts of 76 per cent. alcohol, and 66·5 parts of 55 per cent. alcohol. If free hydrochloric acid is present, 1 part of the salt dissolves in 76 per cent. alcohol. O. Döpping found that the salt is soluble in a soln. of **ammonium succinate;** and C. Claus, very soluble with decomposition in a soln. of **potassium thiocyanate.** W. Knop observed that the salt is soluble in a soln. of **sodium hydroxide;** and E. von Meyer added that a large excess of **potassium hydroxide** liberates an atom of nitrogen per mol. in the form of ammonia, and with a smaller proportion of potassium hydroxide less nitrogen is so evolved. Fulminating platinum is one of the chief products of the action. N. W. Fischer observed that the salt is soluble in a soln. of **stannous chloride;** and J. B. Rogojsky, that it is less soluble in a soln. of **hydrochloroplatinic acid** than it is in water.

M. L. Huggins prepared **tetramethylammonium chloroplatinate,** $(CH_3)_4NPtCl_6$,

and found that the X-radiograms corresponded with a cubic lattice with edge a=12·65 A., and having each platinum atom surrounded by six chlorine atoms at the corners of a regular octahedron, and each nitrogen atom surrounded by four carbon atoms at the corners of a regular tetrahedron. The distance of the Pt-Cl atoms apart is 2·35 A., if that of the N-C atoms is assumed to be 1·47 A.

J. Thiele [20] prepared **hydrazinium chloroplatinate,** $(N_2H_5)_2PtCl_6$, by mixing a soln. of platinic chloride in absolute alcohol with a conc. aq. soln. of hydrazine hydrochloride and precipitating with absolute ether, washing with the ether, and drying in vacuo. The yellow salt is stable, and dissolves in water with effervescence. E. Herlinger [21] prepared **propylammonium chloroplatinate,** $\{N(C_3H_7)_4\}_2PtCl_6$.

J. J. Berzelius [22] observed that **potassium chloroplatinate,** K_2PtCl_6, is precipitated as a lemon-yellow, crystalline powder on mixing an aq. soln. of platinic chloride with a soln. of potassium hydroxide or of a potassium salt. W. A. Noyes and H. C. P. Weber evaporated 500 c.c. of a soln. of hydrochloroplatinic acid, produced from about 120 grms. of platinum, and contained in a glass-stoppered flask in a current of chlorine, until the liquid occupied about 250 c.c. It was then filtered and diluted to about a litre, and poured in a fine stream into a soln. of about one-third more than the theoretical quantity of potassium chloride, keeping the liquid agitated by a current of air. The precipitate was washed successively in water, alcohol, and ether, and dried by gradually raising the temp. to 400° in a current of air dried by conc. sulphuric acid and phosphorus pentoxide. It can be obtained having a high degree of purity by the methods employed by K. Seubert, W. Halberstadt, or E. H. Archibald for the corresponding ammonium salt—*vide supra.* J. S. Stas also described the preparation of the salt having a high degree of purity. The need for the removal of the last traces of nitric acid from the soln. before adding the potassium chloride was discussed by H. Precht and co-workers. E. H. Archibald and co-workers, A. F. Holleman, R. Fresenius, W. A. Noyes and H. C. P. Weber, and W. Dittmar and J. McArthur ; the most suitable washing liquid, by H. Precht and co-workers, R. Finkener, D. Lindo, L. Tietjens and B. Apel, A. H. Allen, B. Sjollema, A. Atterberg, and H. Fresenius ; and the most suitable conditions for drying the salt, by A. L. Winton, R. Ruer, R. Fresenius, F. T. B. Dupré, C. G. Eggertz and L. F. Nilson, and G. Krause. The preparation of the salt was discussed by P. Rudnick ; the composition by A. Vürtheim ; the structure by T. M. Lowry ; and the relative stability by H. I. Schlesinger and R. E. Palmeteer.

Potassium chloroplatinate varies in colour from a lemon-yellow to orange-yellow. According to A. L. Winton, the slow evaporation of dil. soln. yields large crystals, and conc. soln. yield a fine powder. The crystals belong to the cubic system, and are usually octahedral though they may appear in thin plates and rod-like forms. The (111)-cleavage is well defined. The crystals were studied by R. Reinicke, G. B. Naess and O. Hassel, F. J. Ewing and L. Pauling, J. E. Lennard-Jones and B. M. Dent, P. P. Ewald, W. Biltz, and N. Wooster. According to P. Stoll, the X-radiograms correspond with a face-centred, cubic lattice with the parameter a=9·64 A. ; G. Engel gave 9·725 A. There are four molecules in a unit cell arranged as indicated in Fig. 82. The atoms of platinum are face-centred in the elementary cell ; the 8 atoms of potassium are arranged at the corners of a cube so that they appear about the platinum atoms as if on a sphere with radius 4·17 A. ; and the 6 atoms of chlorine are arranged at the corners of an octahedron about each atom of platinum at a distance 2·48 A. W. A. Frederikse and H. J. Verweel gave 2·29 A. The calculated ionic radii are : for platinum, 0·73 A. ; for potassium, 1·80 A.; and for chlorine, 1·75 A. Observations were made by M. Mathieu. The sp. gr. found by G. Tschermak is 3·694 ; H. Schröder, 3·344 ; C. H. D. Bödeker, 3·586 ; E. H. Archibald, 3·499 at 24°/4° ; and R. Klement, 3·474 at 25°/4°, and for the mol. vol. 140·0. R. Romanis discussed the mol. vol. I. Traube found that at 20°/4°, soln. with 0·874, 0·919, and 0·930 per cent. of potassium chloroplatinate had the respective sp. gr. 1·00408, 1·00445, and 1·00457, and the respective mol. soln. vol., 163·5, 159·9, and 157·6. G. B. Naess and

O. Hassel studied the interatomic distances. F. Rüdorff found that measurements of the rate of diffusion agree with the assumption that in aq. soln. KCl and $PtCl_4$ are formed. H. W. Hake exposed $K_2PtCl_6.6H_2O$ to air and observed that deliquescence continued till it had absorbed 15 mols. more of water. E. H. Archibald observed that the purified salt can be heated to 400° in dry air without decomposition, but a specimen prepared from an aqua regia soln. was found by W. A. Noyes and H. C. P. Weber to be decomposed at 250°. J. J. Berzelius observed that when strongly heated the salt is decomposed to form a mixture of platinum and potassium chloride. V. A. Jacquelain found that when the salt is heated to a temp. a little below its m.p., it is partially decomposed, and the separated platinum remains as a black powder when the product is washed with water; if the salt be fused for an hour, the whole of the platinum forms shining laminæ possibly owing to the welding of the grains of powder, as the potassium chloride volatilizes, the laminæ of platinum unite to form a network of metal, but decomposition is incomplete even after the salt has been kept in a molten state for a long time. G. Gire observed that dissociation begins at about 600°, and below 774°, the m.p. of potassium chloride, the heat of the reaction is 38·6 Cals. and above that temp., 46·0 Cals. The vap. press., p, in mm. of mercury, is:

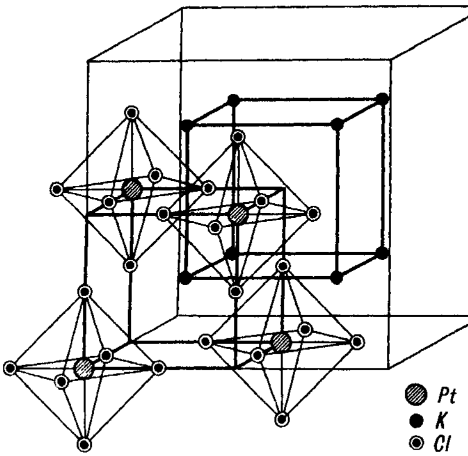


FIG. 82.—The Space-Lattice of Potassium Chloroplatinate, K_2PtCl_6.

	607°	656°	708°	747°	801°	854°	921°
p . .	4·4	12·5	39·2	84·6	245	681	1750

H. Kopp gave 0·120 for the mol. ht., and the subject was studied by J. Maydel. J. Thomsen gave for the heat of formation (Pt, $2Cl_2$, 2KCl)=89·0 Cals.; and from a soln. of K_2PtCl_4 and chlorine gas, 47·9 Cals.; and (Pt, $2Cl_2$, 2KCl, Aq.)=84·62 Cals.; L. Pigeon gave ($PtCl_4$, 2KCl)=29·7 Cals. in the solid state, and 23·53 Cals. in aq. soln. J. Thomsen gave −13·76 Cals. for the heat of solution. N. S. Kurnakoff found that the index of refraction of a 13·375 per cent. soln., and of sp. gr., 1·11225 at. 17·2°/4°, is 1·34770 in Li-light, and 1·35021 in Na-light. This gives 80·5 for the mol. refraction for Na-light, and with the μ-formula; and the corresponding at. refraction of platinum is 24·7. L. Raiteri gave 1·8103 for λ=677; 1·8209 for λ=606; 1·8353 for λ=535; and 1·8560 for λ=458. J. Lifschitz and E. Rosenbohm studied the optical properties. O. Stelling examined the X-ray spectrum. R. Samuel and co-workers, A. Hantzsch, and H. I. Schlesinger and M. W. Tapley studied the absorption spectrum; and O. Stelling and F. Olsson, and S. Aoyama and co-workers, the X-ray spectrum. P. Walden gave for the eq. electrical conductivity, λ, of a soln. of a gram-equivalent in v litres:

v . .	32	64	128	256	512	1024
λ . .	108·5	114·4	119·1	122·7	125·7	125·4

J. A. Prins and R. Fontayne, S. Nagami, and A. Werner and A. Miolati also made some observations on this subject; and E. R. Smith measured the potential of the chloroplatinate-chloroplatinite electrode. E. Feytis found the magnetic susceptibility to be $-0·393\times10^{-6}$ mass unit. E. Rosenbohm studied the subject.

The salt was analyzed by K. Seubert, J. J. Berzelius, W. Halberstadt, M. Vèzes, and W. Dittmar and J. McArthur. K. Seubert always obtained a little water

when the salt is reduced in hydrogen. W. Dittmar and J. McArthur said that the trace of water which the salt contains may be present as hydroxide and not as absorbed water or water of crystallization. J. S. Stas said that the salt can be prepared "absolutely" free from water if obtained precipitated from very dil. soln., and, according to E. H. Archibald, the salt dried at 400° is free from water. The constitution of the salt was discussed by J. A. N. Friend, and S. H. C. Briggs. According to J. J. Berzelius, and R. Finkener, the salt is completely reduced to platinum when it is heated in **hydrogen.** P. Vallet said that reduction by hydrogen commences at 160°, and it is complete at 300°. The salt is sparingly soluble in cold **water,** but more soluble in hot water, forming a pale yellow liquid. W. Crookes found that 100 parts of water dissolve 0·926 part of salt at 15°, and 5·26 parts at 100°. G. Kirchhoff and R. Bunsen found the solubility, S grms. of salt per 100 grms. of water, to be :

	0°	10°	20°	30°	40°	50°	60°	80°	100°
S . .	0·74	0·90	1·12	1·41	1·76	2·17	2·64	3·79	5·18

and E. H. Archibald and co-workers gave :

	2°	16°	25°	35°	48°	59°	68°	78°	92°
S .	0·4812	0·6718	0·8641	1·132	1·745	2·396	2·913	3·589	4·484

N. Demassieux and J. Heyrovsky studied the dissociation of the salt in soln. According to W. A. Noyes and H. C. P. Weber, and E. H. Archibald and co-workers, the aq. soln. slowly acquires an acidic reaction at ordinary temp., and more rapidly when boiled. The results of E. H. Archibald and W. A. Gale are summarized in Fig. 83. E. Sonstadt observed that heating a soln. of 1 part of the salt in 1000 parts of water produces no perceptible change in 1 to 2 hrs., a soln. of 1 part of the salt in 10,000 parts of water becomes turbid almost at once, and almost opaque after it has stood for a few hours. If the soln. be heated for some days, adding water from time to time, a precipitate is formed, and the liquid is clear. It is suggested that the hydrolysis is initiated by the salt dissociating into platinic and potassium chlorides, and the water then attacks the platinic chloride. Exposing the aq. soln. to sunlight also hastens the hydrolysis as in the case of heat. J. Fiedler observed that a soln. of potassium chloroplatinate is reduced to platinum by exposure to sunlight. A. von Schrötter said that potassium chloroplatinate is less soluble in a soln. of **potassium chloride** than it is in water, and nearly insoluble in a sat. soln. of potassium chloride, so that O. W. Gibbs could say that it is insoluble in a soln. of potassium chloride. E. H. Archibald gave for the solubility, S grms. K_2PtCl_6 in 100 grms. of soln. containing [KCl] mols of potassium chloride per litre, at 20° :

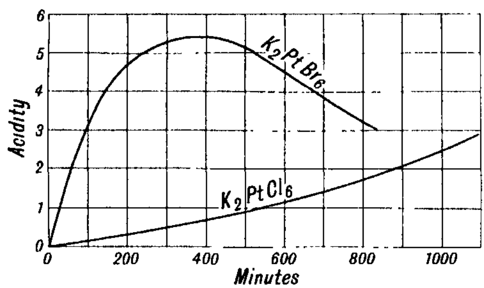


FIG. 83.—The Hydrolysis of Potassium Chloroplatinate and Bromoplatinate.

[KCl] .	0·00	0·20	0·25	0·50	1·0	2·0	4·0	Sat.
S . .	0·7742	0·0236	0·0207	0·0109	0·0046	0·0045	0·0042	0·0034

The solubility decreases with increasing concentration of potassium chloride, but increases with increasing concentration of **sodium chloride**—Fig. 84. The data for sodium chloride at 16° are :

[NaCl] .	0·00	0·05	0·10	0·25	0·50	0·75	1·00	2·00
S . .	0·672	0·700	0·729	0·758	0·775	0·791	0·805	0·834

A. von Schrötter observed that potassium chloroplatinate is slightly soluble in cold, dil. acids ; but it is more soluble when the temp. is raised. W. Dittmar

and J. McArthur observed that 100 parts of water dissolve 0·628 part of the salt; of 5 per cent. **hydrochloric acid,** 0·662 part; of 5 per cent. soln. of **platinic chloride,** 0·233 part; of a soln. of platinic chloride containing 0·05 grm. free HCl, and 0·05 grm. of platinum per c.c., 0·168 part; and of **sulphuric acid,** containing 40 grms. SO_3 per litre, 0·900 part. L. Tschugaeff and S. Krassikoff studied the action of sulphur dioxide. J. L. Lassaigne said that the salt is not attacked by cold, conc. sulphuric acid. C. Himly found that potassium chloroplatinate is readily dissolved by a soln. of **sodium thiosulphate** that contains a little sodium hydroxide. A. Minozzi observed that a **selenite** reduces the soln. to form platinum selenide. According to W. Peters, potassium chloroplatinate does not absorb dry **ammonia,** but it combines with **methylamine** to form **potassium dodeciesmethylamine-chloroplatinate,** $K_2PtCl_6.12CH_3NH_2$, and with **dimethylamine** to form **potassium sexiesdimethylaminechloroplatinate,** $K_2PtCl_6.6(CH_3)_2NH$. A soln. of **ammonium chloride** was found by R. H. Brett to dissolve potassium chloroplatinate; A. L. Winton and H. J. Wheeler observed that the action is very small; and H. Haefcke, and R. Finkener noted that the effect produced depends on the duration of the attack, and the temp. P. Jannasch and C. Stephan observed

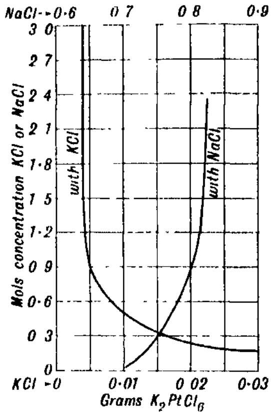


FIG. 84.—The Effect of Potassium and Sodium Chlorides on the Solubility of K_2PtCl_6.

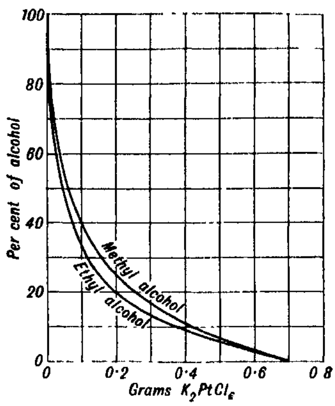


FIG. 85.—The Solubility of K_2PtCl_6 in Methyl and Ethyl Alcohols.

that **hydrazine hydrate** precipitates platinum quantitatively from a boiling soln. M. Vèzes found that a hot, dil. soln. of the salt dissolves in a soln. of **potassium nitrite,** forming a yellow liquid which when heated gives off nitrous fumes, and possibly contains $K_2Pt(NO_2)Cl_5$; and also **potassium tetranitrito-platinite,** $K_2Pt(NO_2)_2Cl_2$ is formed.

P. Rohland said that potassium chloroplatinate is insoluble in **ether,** and in **methyl alcohol;** M. Péligot, that a litre of methyl alcohol at 20° dissolves 0·072 grm. of the salt; and E. H. Archibald and co-workers, that the solubility, *S* grm. of K_2PtCl_6 in 100 grms. of soln., at 20°, with methyl alcohol containing different proportions of water, Fig. 85, is as follows:

CH_3OH .	0	5	10	20	40	60	80	100 per cent.
S . .	0·7742	0·5350	0·4120	0·2642	0·1165	0·10325	0·0124	0·0027

H. Precht observed that 1 part of the salt dissolves in 42,600 parts of absolute **ethyl alcohol;** 37,300 parts of 96 per cent. alcohol; and 26,400 parts of 80 per cent. alcohol; and R. Fresenius, that at 15° to 20°, 1 part of the salt dissolves in 12,083 parts of absolute alcohol; in 3775 parts of 76 per cent. alcohol; in 1053 parts of 55 per cent. alcohol; in 1835 parts of 76 per cent. alcohol containing hydrogen chloride. Measurements were also made by M. Péligot, and M. Pierrat. E. H. Archibald and co-workers found that the solubility, *S* grm. of K_2PtCl_6 in

100 grms. of soln., at 20°, with ethyl alcohol containing different proportions of water, Fig. 85, is as follows :

C_2H_5OH .	0	5	10	20	40	60	80	100 per cent.
S . .	0·7742	0·4910	0·3720	0·2180	0·0760	0·0265	0·0085	0·0009

The solubilities in **isobutyl alcohol** saturated with water, and also with 91·8 per cent. of water, are, respectively, 0·6250 and 0·3180 grm. of K_2PtCl_6 per 100 grms. of soln. R. Finkener said that potassium chloroplatinate is less soluble in a mixture of alcohol and ether than it is in alcohol alone, and hence R. Finkener, and B. C. Corenwinder and G. Contamine recommended a mixture of the two for washing the precipitated salt; and H. N. Warren proposed using a mixture of **amyl alcohol** and ether. O. Döpping found that the salt is soluble in a soln. of **ammonium succinate.** Potassium chloroplatinate was found by A. Atterberg to be reduced to metal by **thioacetic acid ;** by H. N. Warren, by **formic acid ;** by R. Böttger, M. Woussen, F. Jean and J. A. Trillat, and B. C. Corenwinder and A. Contamine, by **sodium formate ;** by L. L. de Koninck, by **calcium formate ;** and by F. Mohr, by **sodium oxalate.**

The reduction of potassium chloroplatinate to metal by **zinc** dust was noted by J. Diamant; by **mercury,** by E. Sonstadt; by **magnesium** ribbon, by L. L. de Koninck, C. Favre, A. Villiers and F. Borg, A. Fiechter, R. Trnka, and A. Atterberg; and by finely-divided **cobalt,** by L. Pigeon. W. F. Hillebrand noted a reaction between the **platinum** of the evaporating dish, and a soln. of the salt. H. Rose noted that the salt is soluble in soln. of **potassium hydroxide,** and that when a mixture of the salt with potassium hydroxide and a little water is heated, some platinum dioxide is formed. The hot sat. soln. in potash-lye on cooling and the addition of hydrochloric acid deposits the chloroplatinate. The salt is insoluble in hot or cold soln. of **alkali carbonates or hydrocarbonates.** A. Mercier found that the salt is reduced to metal by **mercurous chloride.**

A. Cossa prepared **potassium amminopentachloroplatinate,** $K[Pt(NH_3)Cl_5].H_2O$, by oxidizing an acidified soln. of potassium amminotrichloroplatinite with potassium permanganate, or chlorine, and evaporating the liquor on a water-bath; and by the action of chlorine, on $[Pt(NH_3)Cl_3]_2[Pt(NH_3)_4]$, separating the insoluble $[Pt(NH_3)_4Cl_2]Cl_2$, and adding potassium chloride to the clear liquor. The yellow, triclinic crystals lose their water at 100°. A. Werner and A. Miolati, S. M. Jörgensen, and S. H. C. Briggs discussed the constitution of the salt. A. Werner and A. Miolati found the conductivity, μ, of the salt in 125 litres to be 108·5, and the values increase with time.

Time . .	1	5	10	20	30	360 min,
μ . .	114·4	130·7	141·6	175·86	190·4	211·8

showing a progressive hydrolysis. If the salt be mixed with platinous tetramminochloride, there is formed the complex **platinous tetramminotetrachloroamminoplatinate,** $[Pt(NH_3)Cl_5]_2Pt(NH_3)_4$. A. Werner and F. Fassbender also prepared **potassium pyridinepentachloroplatinate,** $K[Pt(C_5H_5N)Cl_5]$.

G. Kirchhoff and R. Bunsen prepared **rubidium chloroplatinate,** Rb_2PtCl_6, by adding a soln. of rubidium chloride to one of platinic chloride, and drying the washed precipitate at 150°; and A. Windaus, by pouring a small excess of a conc. soln. of platinic chloride into a soln. of a rubidium salt in a little alcohol acidified with hydrochloric acid, then adding alcohol, filtering the mixture by suction, washing with alcohol, and drying at 105°. The pale yellow powder contains regular octahedra. G. Natta and R. Pirani examined the X-radiogram, and found that the cubic cell has a=9·83 A.; a volume $949·85\times10^{-24}$ c.c., and that there are 4 mols. per unit cell. The density is 4·04. G. Engel gave a=9·882 A., and density 3·957. G. B. Naess and O. Hassel studied the lattice constants; and G. Kirchhoff and R. Bunsen found that hydrogen partially removes the chlorine from the platinum in the cold, and reduction is complete when the salt is heated. The salt is less soluble in water than the potassium salt; W. Crookes said that

100 parts of water at 15° dissolve 0·135 part of salt, and at 100°, 0·637 part; and G. Kirchhoff and R. Bunsen measured the solubility of the salt, and E. H. Archibald and L. T. Hallett's results are indicated below. The minimum at 14° shows that the salt forms a hydrate. W. Peters observed that the salt does not absorb dry ammonia. A. Werner and F. Fassbender prepared **rubidium pyridinepentachloroplatinate,** $Rb[Pt(C_5H_5N)Cl_5]$. G. Kirchhoff and R. Bunsen, and A. Windaus prepared **cæsium chloroplatinate,** Cs_2PtCl_6, by the methods employed for the rubidium salt. The pale yellow powder consists of microscopic, regular octahedra, which are less soluble in water than the rubidium salt. E. H. Ducloux examined the crystals of the salt; G. B. Naess and O. Hassel, the lattice constants. G. Engel gave a=10·192 A. for the cubic crystals. W. Crookes observed that 100 parts of water at 15° dissolve 0·076 part of salt, and at 100°, 0·383 part; and G. Kirchhoff and R. Bunsen measured the solubility of the cæsium salt. The solubility—S grms. of salt per 100 grms. of water—of the rubidium and cæsium salts, determined by E. H. Archibald and L. T. Hallett, were:

	0°	10°	20°	40°	60°	80°	100°
Rb_2PtCl_6 . .	0·0137	0·0200	0·0283	0·0565	0·0997	0·1824	0·3340
Cs_2PtCl_6 . .	0·0047	0·0064	0·0086	0·0158	0·0290	0·0525	0·0915

G. Natta and R. Pirani found that the crystals belong to the cubic system and that the X-radiograms indicate that there are 4 mols. per unit cell, and that a=10·15 A.; the volume is $1045·7 \times 10^{-24}$ c.c.; and the density is 4·25. They also studied the solid soln. of rubidium and cæsium chloroplatinates, and of cæsium chloroplatinate and chlorotellurate. G. Engel gave a=10·185 A., and density, 4·205. A. Werner and F. Fassbender prepared **cæsium pyridinepentachloroplatinate,** $Cs[Pt(C_5H_5N)Cl_5]$.

C. Scheibler[23] prepared **lithium chloroplatinate,** $Li_2PtCl_6.6H_2O$, by evaporating conc. soln. of the salt over sulphuric acid. The *hexahydrate* forms orange-yellow, tabular crystals, which lose their water at 180°, and, according to W. Peters, the salt decomposes. C. Scheibler added that the general behaviour of the salt resembles that of the sodium salt; and it is readily soluble in water, alcohol, and a mixture of alcohol and ether, but not in ether. G. F. Smith and A. C. Shead recommended the use of this salt in place of hydrochloroplatinic acid for precipitating potassium. A. Werner and F. Fassbender prepared **lithium pyridinepentachloroplatinate,** $Li[Pt(C_5H_5N)Cl_5].nH_2O$.

L. N. Vauquelin, and A. von Mussin-Puschkin prepared **sodium chloroplatinate,** $Na_2PtCl_6.6H_2O$, by mixing aq. soln. of platinic and sodium chlorides, and evaporating; P. Rohland recommended using theoretical proportions of the two salts. N. S. Kurnakoff and M. I. Ravitsch studied the ternary system: $NaCl-PtCl_4-H_2O$; and T. A. Genke, the mutual solubilities of the component salts, and concluded that sodium chloroplatinate is hydrolyzed in aq. soln. at 25°. S. Nagami found that for soln. with an eq. of $NaHPtCl_6$ in 200, 500, and 1000 litres, at 25°, the conductivities were 497, 511, and 517 respectively. L. F. Nilson, and R. Böttger added sodium carbonate to a soln. of hydrochloroplatinic acid. J. S. Stas noted that some sodium chloroplatinate is formed when sodium chlorate is fused in a platinum vessel. H. Precht purified the dry salt by dissolving it in hot alcohol when sodium chloride remains undissolved. The *hexahydrate* appears in aurora-red columns or plates, or as an orange-red powder. M. Delépine and P. Boussi studied the hydrates. P. Rohland, and H. Töpsöe obtained triclinic needles, and J. C. G. de Marignac, triclinic pinacoids with the axial ratios $a:b:c$=0·9625 : 1 : 0·8444, and α=101° 56′, β=128° 2′, and γ=72° 6′, as given by P. Groth. H. Töpsöe gave 2·500 for the sp. gr., and 226·0 for the mol. vol. H. Precht gave 1·368 for the sp. gr. of a sat. soln. containing 39·77 per cent. of salt at 15°. B. L. Vanzetti measured the rate of diffusion of the salt in aq. soln., and in gelatin; and F. Rüdorff observed that the diffusion experiments indicate that sodium chloroplatinate behaves like a double salt in aq. soln.

According to L. N. Vauquelin, the hexahydrate loses all its water of hydration when carefully heated, and leaves the anhydrous salt as an orange-yellow powder. H. Precht said that the hexahydrate loses most of its water at about 100°. J. C. G. de Marignac observed that the water is expelled at 100°, W. Peters at 150°, and J. Thomsen at 150° to 160°. M. A. Rakuzin studied the subject. The anhydrous chloroplatinate was found by L. N. Vauquelin to swell up when more strongly heated, but it requires a fairly high temp. for its complete decomposition into platinum and sodium chloride. L. Wöhler and P. Balz observed no evidence of the formation of complexes of univalent or tervalent platinum in the thermal decomposition of the salt; the chloroplatinate is stable below 600°, and above 800°, only the chloroplatinite is formed. G. Gire noted that the heat of formation is 40·6 Cals., and the vap. press., p, in mm. of mercury is:

	503°	548°	601°	651°	694°	720°	758°
p . . .	6·0	23·2	64·4	252	605	848	1450

F. M. Raoult found that the lowering of the f.p. of aq. soln. indicates that in a soln. of a mol of the salt in 4 litres of water, about a quarter of a mol. is dissociated. L. Pigeon gave for the heat of formation ($PtCl_4$, $2NaCl$)=13·9 Cals. for the solid, and 25·29 Cals. for the aq. soln. J. Thomsen gave (Pt, $2Cl_2$, $2NaCl$)=73·72 Cals.; (Pt, $2Cl_2$, $2NaCl$, $6H_2O$)=92·89 Cals.; (Pt, $2Cl_2$, $2NaCl$, Aq.)=84·62 Cals.; and for the reaction between gaseous chlorine and an aq. soln. of sodium chloroplatinite, 43·03 Cals.; V. F. Miller and H. Terry, 40·88 Cals.; J. Thomsen, for the heat of crystallization, 19·17 Cals., or an average of 3·195 Cals. for each mol. of water, when the observed values are 4·32 Cals. each for the first and second mols, 2·54 Cals. each for the third and fourth mols, and 2·725 Cals. each for the fifth and sixth mols. The heat of solution of the anhydrous salt is 8·54 Cals., and for the hexahydrate, −10·634 Cals., or for the hydrates:

	1	2	3	4	5
H_2O . .	1	2	3	4	5
Cals. . .	+4·220	−0·100	−2·640	−5·180	−7·905

E. Doumer found the refractive index to be 0·267 when the value for water is unity; and N. S. Kurnakoff gave for a 29·123 per cent. soln., and sp. gr. 1·28259, the refractive indices 1·38749 for Li-light, and 1·39085 for Na-light; and the mol. refraction for Na-light with the μ-formula is 106·5. This makes the at. refraction of platinum to be 16·1 and 21·0. According to A. Hantzsch and co-workers, eq. soln. of hydrochloroplatinic acid, and of sodium chloroplatinate in the same solvent are optically identical, that is, show the same absorption spectrum, and the molecular absorption is independent of the degree of ionization. The light absorption of the acid and of the salt is also unaffected by changes of temperature. The solvent does not appear to exercise any influence on the absorption in the blue and violet parts of the spectrum, but does so to a very slight extent in the green and ultra-violet. J. Fiedler observed that a soln. of sodium chloroplatinate is reduced to platinum by exposure to sunlight. L. Pigeon found that the electrical conductivity of a soln. of 0·01 mol of salt in a litre of water is 1·830.

A. von Mussin-Puschkin said that the hexahydrate is freely soluble in **water**, and J. Thomsen made a similar observation with respect to the anhydrous salt. H. Precht found that a soln. sat. at 15° contains 39·77 per cent. of Na_2PtCl_6, and that in boiling water it dissolves in almost all proportions. T. A. Henke found that the salt is hydrolyzed in aq. soln. G. Sailer observed that sodium thiosulphatoplatinite is ultimately formed by the action of **sodium hyposulphite**.

W. Peters observed that the dehydrated salt takes up dry **ammonia** to form **sodium hexamminochloroplatinate,** $Na_2PtCl_6.6NH_3$, and that this ammine, in vacuo, forms **sodium pentamminochloroplatinate,** $Na_2PtCl_6.5NH_3$. Sodium chloroplatinate also unites with **methylamine** to form **sodium dodeciesmethylaminechloroplatinate,** $Na_2PtCl_6.12CH_3NH_2$; and with **dimethylamine** to form **sodium sexiesdimethylaminechloroplatinate,** $Na_2PtCl_6.6(CH_3)_2NH$. A. von

Mussin-Puschkin observed that **ammonium chloride** precipitates ammonium chloroplatinate from the soln. of the sodium salt, and sodium chloride remains in soln.

The hexahydrate was found by A. von Mussin-Puschkin to be freely soluble in **alcohol,** and H. Precht observed that it is more soluble in absolute alcohol than it is in aq. alcohol. M. Péligot's measurements of the solubility of the salt in alcohol are summarized in Fig. 86. H. Precht observed that alcohol precipitates the salt from a sat., aq. soln., and that a sat. soln. in absolute alcohol contains 11·9 per cent. of salt. The solubility in 95 per cent. alcohol is 6·34 per cent., and in 90 per cent. alcohol at 15°, 5·35 per cent., and at 55°, 27·15 per cent. A soln. in absolute alcohol contains 48·3 per cent. of dehydrated salt, and on adding a drop of water to the liquid, the mass solidifies as the hexahydrate is formed. On cooling a soln. of the salt in 99·2 per cent. alcohol, a mixture of the anhydrous and hexahydrated salt separates out. J. Dalietos and C. G. Makris found alcohol vapour is readily oxidized by sodium but not by potassium chloroplatinate. H. Precht observed that the salt is precipitated by **ether** from the sat. aq. soln. at 15°; and a mixture of equal parts of alcohol and ether dissolves 2·43 per cent. of the hexahydrate. P. Rohland, and H. Precht said that the salt is insoluble in ether free from alcohol. A. Werner and F. Fassbender prepared **sodium pyridinepentachloroplatinate,** $Na[Pt(C_5H_5N)Cl_5]$.

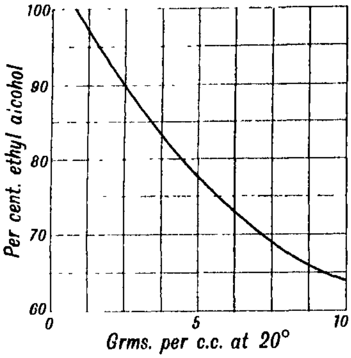


FIG. 86.—The Solubility of Sodium Chloroplatinate in Ethyl Alcohol.

L. Pigeon observed that finely-divided **cobalt** reduces the salt and platinum is formed. A. von Mussin-Puschkin reported that **sodium** or **potassium hydroxide** or **carbonate** forms with a soln. of sodium chloroplatinate a precipitate which dissolves in an excess of the alkali. E. H. Archibald and co-workers discussed the action of **potassium chloride** illustrative of the balanced reaction: $K_2PtCl_6+2NaCl \rightleftharpoons Na_2PtCl_6+2KCl$, exemplified by the effect of sodium chloride on the solubility of potassium chloroplatinate—*vide supra.* W. Ostwald found that the theoretical proportion of **silver nitrate** precipitates silver chloroplatinate quantitatively.

P. A. von Bonsdorff[24] prepared **copper chloroplatinate,** $CuPtCl_6.6H_2O$, by the spontaneous evaporation of a mixed soln. of the constituent salts over sulphuric acid. The pale, olive-green crystals of the *hexahydrate* resemble those of the magnesium salt. H. Töpsöe observed that the needles or prisms are trigonal, with the axial ratio $a : c=1 : 0·5219$, and $\alpha=112° 2'$. The sp. gr. is 2·734, and the mol. vol. 212·8. L. Pauling studied the crystals. According to P. A. von Bonsdorff, the crystals effloresce to a greenish-grey powder over sulphuric acid; they are stable in the dry winter's air, but deliquesce in the humid air of summer. H. Töpsöe observed that 4 mols. of water are given off at 110°; and W. Peters said that the salt becomes anhydrous at 180°, and it is then dark brown, and absorbs dry ammonia to form **copper octodecamminochloroplatinate,** $CuPtCl_6.18NH_3$, which in vacuo forms copper hexamminochloroplatinate, $CuPtCl_6.6NH_3$. With methylamine, there is formed what are probably **copper duodeviciesmethylaminechloroplatinate,** $CuPtCl_6.18CH_3NH_2$; and **copper quinquiesmethylaminechloroplatinate,** $CuPtCl_6.5CH_3NH_2$; with dimethylamine there is formed **copper duodeciesdimethylaminechloroplatinate,** $CuPtCl_6.12(CH_3)_2NH$; and **copper sexiesdimethylaminechloroplatinate,** $CuPtCl_6.6(CH_3)_2NH$; and with trimethylamine, **copper bistrimethylaminechloroplatinate,** $CuPtCl_6.2(CH_3)_3N$. W. Peters observed that when copper chloroplatinate is boiled with formaldehyde or formic acid, traces of platinum are formed.

G. Gore[25] obtained evidence of the formation of a **silver chloroplatinate,**

Ag_2PtCl_6, by melting silver chloride in an atm. of chlorine in a platinum vessel. L. N. Vauquelin obtained a yellow precipitate by adding silver nitrate to a soln. of hydrochloroplatinic acid, and J. E. Herberger said that ammonia extracts only a part of the silver chloride contained in the precipitate. K. Birnbaum found that if silver chloride be dissolved in hydrochloroplatinic acid, the silver salt crystallizes out unchanged when the soln. is evaporated. The salt was prepared by A. Commaille, S. A. Norton, and S. M. Jörgensen. L. Pigeon reported the formation of silver chloroplatinate from a soln. containing the theoretical proportions of silver nitrate and hydrochloroplatinic acid; and A. Miolati added that if an excess of silver nitrate be present, $Ag_2Pt(OH)_2Cl_4$ is formed. According to W. Ostwald, the silver salt is formed quantitatively when the theoretical proportion of silver nitrate is added to a soln. of sodium chloroplatinate. L. Pigeon gave for the heat of formation $(2AgCl, PtCl_4)=7{\cdot}7$ Cals. According to S. M. Jörgensen, and A. Miolati, cold water slowly decomposes the salt, forming silver chloride and $H_2Pt(OH)_2Cl_4$, and with hot water the reaction proceeds rapidly. W. Peters observed that the salt absorbs about 10 mols. of dry ammonia, forming **silver octamminochloroplatinate,** $Ag_2PtCl_6.8NH_3$; and in vacuo, this forms **silver tetramminochloroplatinate,** $Ag_2PtCl_6.4NH_3$; K. Birnbaum obtained **silver diamminochloroplatinate,** $Ag_2PtCl_6.2NH_3$, by mixing freshly-prepared hydrochloroplatinic acid with an ammoniacal silver chloride soln. and washing the yellow product rapidly with cold water, and drying it over sulphuric acid. The salt loses water at 100°, and at a higher temp. forms platinum and silver chloride. It is insoluble in water. Ammonia is evolved when the product is treated with potashlye; when boiled with sodium carbonate, a dirty yellow precipitate is formed containing a part of the silver and part of the platinum.

W. Peters found that when a mixed soln. of auric chloride and hydrochloroplatinic acid is evaporated, no **gold chloroplatinate** is formed since the gold separates out in the metallic state. A. Cahours and H. Gal prepared **platinic quatertriethylphosphinechloroaurate,** $[Pt\{P(C_2H_5)_3\}_4]AuCl_4$.

P. A. von Bonsdorff[26] prepared **calcium chloroplatinate,** $CaPtCl_6.6H_2O$, in small, orange-red prismatic crystals by evaporating a mixture of hydrochloroplatinic acid with an excess of calcium chloride, and separating mechanically the crystals of the *octohydrate* from those of calcium chloride. P. Rohland, and H. Töpsöe prepared the *enneahydrate*, $CaPtCl_6.9H_2O$, by evaporating a soln. of theoretical proportions of the component chlorides over sulphuric acid. L. Pauling found that the crystals of the hexahydrate are rhombohedral with $\alpha=112°\ 0'$. P. A. von Bonsdorff, and W. Peters said that the water can be expelled by heating to 170°, and a yellow powder remains. The crystals of the hydrate are freely soluble in water; H. Precht observed that the sat. alcoholic soln. contains 53 per cent. of salt; P. Rohland added that the salt is soluble in methyl alcohol of sp. gr. 0·790 at 15°, and in ethyl alcohol of sp. gr. 0·8035 at 15°, and the salt is decomposed in soln. into its component chlorides. It is insoluble in ether. W. Peters said that when the anhydrous salt is exposed to dry ammonia it forms **calcium dodecamminochloroplatinate,** $CaPtCl_6.12NH_3$, and that in vacuo, this forms **calcium hexamminochloroplatinate,** $CaPtCl_6.6NH_3$. P. A. von Bonsdorff prepared **strontium chloroplatinate,** $SrPtCl_6.8H_2O$, as in the case of the calcium salt. The rhombic prisms are stable in air, but effloresce in warm air. The salt is freely soluble in water. H. Precht found that the salt is decomposed by absolute alcohol.

A. von Mussin-Puschkin, and P. A. von Bonsdorff also prepared **barium chloroplatinate,** $BaPtCl_6.6H_2O$, by the spontaneous evaporation of a mixed soln. of hydrochloroplatinic acid with an excess of barium chloride. P. Rohland used theoretical proportions of the two constituents. H. Töpsöe added that it is difficult to prevent contamination with barium chloride since there is a slight decomposition of the salt during recrystallization. The salt was also prepared by J. J. Berzelius. The *hexahydrate* forms orange-yellow, monoclinic prisms and plates which, according to H. Töpsöe, have the axial ratios $a:b:c=0{\cdot}9645:1:1{\cdot}4949$, and $\beta=102°\ 15'$.

The (001)-cleavage is perfect; the sp. gr. is 2·868, and the mol. vol. is 216·0. W. Kwasnik obtained the *octohydrate*, $BaPtCl_6.8H_2O$, by the action of hydrochloroplatinic acid on barium oxide, concentrating the filtered soln. on a water-bath, precipitating with absolute alcohol, washing the product, and recrystallizing from aq. soln. The hexahydrate forms the *monohydrate* at 70°, and the anhydrous salt is formed at 100° in a current of dry air. W. Peters said that all the water is lost at 150° to 160°. When heated to a higher temp., platinum and barium chloride are formed. According to G. Gire, the vap. press., p, in mm. of mercury, is:

	428°	458°	514°	556°	607°	655°	721°
p	4·6	9·8	31·2	80·3	210	531	1600

The heat of formation is 40·9 Cals. H. Precht, and H. Töpsöe observed that the salt is partially decomposed in aq. soln., and H. Precht, and P. Rohland, that the salt is almost completely decomposed by methyl alcohol, and by ethyl alcohol. W. Peters observed that the anhydrous salt takes up dry ammonia to form **barium hexamminochloroplatinate,** $BaPtCl_6.6NH_3$, which, in vacuo, forms **barium pentamminochloroplatinate,** $BaPtCl_6.5NH_3$.

J. Thomsen [27] prepared **beryllium chloroplatinate,** $BePtCl_6.8H_2O$, by dissolving beryllium hydroxide, freed from adsorbed ammonium salts by digestion with bromine water, in hydrochloroplatinic acid, and evaporating the soln. for crystallization. A. Welkow evaporated a mixture of conc. soln. of beryllium and platinic chlorides slowly over conc. sulphuric acid. The crystals are dark yellow, being four- or six-sided prisms, or six- or eight-sided plates. According to J. C. G. de Marignac, the crystals belong to the tetragonal system; and they were examined by K. Haushofer. A. Welkow, and J. Thomsen said that the crystals of the *octohydrate* are stable in dry air, but deliquesce in moist air; they lose 4 mols. of water at 100° to 120°, and above 150° water and hydrogen chloride are given off. The salt is freely soluble in water, and alcohol, but insoluble in ether.

H. Töpsöe,[28] and A. von Mussin-Puschkin prepared **magnesium chloroplatinate,** $MgPtCl_6.12H_2O$, by evaporating a soln. of the component salts, at a low temp. H. Töpsöe, and H. Töpsöe and C. Christiansen observed that the dark reddish-yellow crystals of the *dodecahydrate* are trigonal with the axial ratio $a:c=1:0·7057$, and $\alpha=106°\ 39'$; the crystals are birefringent. The sp. gr. is 2·060, and the mol. vol. 315·3. The crystals are stable in air, but pass into the *hexahydrate* at 100°. L. Pauling studied the crystals. P. A. von Bonsdorff obtained the hexahydrate by the spontaneous evaporation of an aq. soln. of the component salts, and H. Töpsöe added, at a temp. higher than that needed for the dodecahydrate; it is also obtained by slowly cooling a sat. soln. down to about 20°. H. Precht found that the salt cannot be purified by recrystallization. H. Töpsöe observed that the pale yellow crystals are trigonal, with the axial ratio $a:c=1:0·5169$, and $\alpha=112°\ 10'$; the sp. gr. is 2·437, and the mol. vol. 222·5. P. Gaubert found the refractive indices vary with the moisture content; and for the *heptahydrate*, for sodium light, $\omega=1·561$, and $\epsilon=1·91$. P. A. von Bonsdorff said that the crystals are stable in air, but H. Töpsöe found that the crystals rapidly absorb moisture to form a pale yellow powder. According to P. A. von Bonsdorff, the crystals lose 4 mols. of water when heated. H. Precht found that the hexahydrate dissolves in absolute alcohol forming a sat. soln. with 43·2 per cent. of $MgPtCl_6$, but with the salt dried at 150°, the soln. contains only 37·8 per cent. P. Rohland added that the salt is soluble in 80 per cent. alcohol of sp. gr. 0·8055 at 15°; and in methyl alcohol of sp. gr. 0·790 at 17°, but it is insoluble in ether. The alcoholic soln. suffers some dissociation, forming magnesium chloride.

L. Hünefeld prepared **zinc chloroplatinate,** $ZnPtCl_6.6H_2O$, by treating a soln. of platinum in aqua regia with zinc until the soln. acquires a pale yellow colour, and evaporating the filtrate; the first crop of crystals is the chloroplatinite, and the later crop, chloroplatinate. A. Eberhard said that the crystals are red. P. A. von Bonsdorff obtained the salt by crystallization from a mixed soln. of the

two component chlorides. L. Hünefeld said that the crystals of the *hexahydrate* are pale yellow, and H. Töpsöe described them as orange-yellow prisms belonging to the trigonal system, with the axial ratio $a : c$, and $\alpha=112° \ 10'$. The $(10\bar{1})$-cleavage is perfect. H. Töpsöe and C. Christiansen discussed the positive birefringence. L. Pauling studied the crystals. P. A. von Bonsdorff found the crystals to be isomorphous with those of the hydrated magnesium and manganese chloroplatinates. S. M. Jörgensen gave 2·717 for the sp. gr. R. Romanis discussed the mol. vol. L. Hünefeld said that when heated, the salt loses water becoming brown and then grey; W. Peters added that the salt is anhydrous and brown when heated to 160°. A. Eberhard said that the crystals lose "$4H_2O$" at 102° to 103°; and the remaining "$2H_2O$" is lost slowly above 130°; P. A. von Bonsdorff, that at a high temp., chlorine is evolved, zinc chloride is sublimed, and platinum remains. L. Hünefeld reported that the salt deliquesces in air; but P. A. von Bonsdorff, and H. Töpsöe said not so. The salt was found by L. Hünefeld to be easily soluble in water, and alcohol; and to be easily decomposed with the evolution of chlorine and hydrogen chloride when it is treated with sulphuric acid. W. Peters observed that the anhydrous salt takes up dry ammonia to form **zinc enneamminochloroplatinate,** $ZnPtCl_6.11NH_3$, which in vacuo forms **zinc heptamminochloroplatinate,** $ZnPtCl_6.7NH_3$. P. A. von Bonsdorff, and H. Töpsöe prepared **cadmium chloroplatinate,** $CdPtCl_6.6H_2O$, as in the case of the magnesium salt. The pale yellow crystals of the *hexahydrate* were found by H. Töpsöe, and H. Töpsöe and C. Christiansen to be isomorphous with the zinc salt, and to furnish trigonal crystals with the axial ratio $a:c=1:0·5335$, and $\alpha=112° \ 0'$. The (101)-cleavage is complete; the birefringence is positive; the sp. gr. is 2·882; and the mol. vol. 218·7. The crystals are stable in air at ordinary temp., and become anhydrous at 100°. W. Peters obtained the *trihydrate* in the form of pale yellow needles, which become grey at 170°. W. Peters observed that the anhydrous salt takes up dry ammonia to form **cadmium heptadecamminochloroplatinate,** $CdPtCl_6.17NH_3$; and this in vacuo forms **cadmium duodecamminochloroplatinate,** $CdPtCl_6.12H_2O$. By boiling the aq. soln. with formaldehyde, or formic acid, a trace of platinum is deposited.

P. A. von Bonsdorff observed that mercurous chloride dissolves in warm hydrochloroplatinic acid, and that crystals, possibly **mercurous chloroplatinate,** are formed on cooling; but K. Birnbaum found that mercurous chloride acts on hydrochloroplatinic acid, forming a soln. which on evaporation deposits a crop of crystals of mercuric chloride, then a deliquescent amorphous mass containing mercuric and platinic chlorides which with aq. ammonia, produces a pale yellow deposit containing mercury, platinum, and ammonia. L. F. Nilson said that a mixed soln. of mercuric and platinic chlorides does not furnish **mercuric chloroplatinate.**

W. F. Salm-Horstmar,[29] and A. Welkow prepared **aluminium chloroplatinate,** $AlPtCl_7.15H_2O$, by evaporating over sulphuric acid a mixture of hydrochloroplatinic acid and a soln. of aluminium in hydrochloric acid, and pressing the crystals between bibulous paper. The lemon-yellow, or orange-yellow four- or six-sided columns or plates are triclinic with the axial ratios $a : b : c=1 : 0·6418 : 0·5373$, and $\alpha=92° \ 0'$, $\beta=91° \ 35'$, and $\gamma=90° \ 50'$. The crystals are stable in dry air, but deliquesce in moist air. When heated, the crystals become black, and on cooling, red; the m.p. and f.p. are 52°; the salt loses 12 mols. of water at 120°, and the remainder, with decomposition, at 200°. The salt is freely soluble in water, and alcohol, but it is not soluble in ether. Platinum is deposited when a soln. of the salt is treated with zinc. L. F. Nilson reported **indium chloroplatinate,** $2InCl_3.5PtCl_4.36H_2O$, to be formed by evaporating to dryness a mixture of 2 molar parts of hydrochloroplatinic acid, and 1 molar part of a soln. of indium oxide in hydrochloric acid, dissolving the product in water and crystallizing the soln. over sulphuric acid, and drying the crystals between bibulous paper. The honey-yellow, prismatic crystals deliquesce rapidly in air; they melt at 100°, and lose 18 mols. of water. F. Kuhlmann, and W. Crookes obtained pale yellow crystals of **thallous chloro-**

platinate, $TlPtCl_6$, by adding hydrochloroplatinic acid to a dil. soln. of a thallous salt. One hundred parts of water at 15° dissolve 0·00638 part of salt, and at 100°, 0·0513 part. G. Engel gave a=9·755 A. for the cubic lattice. G. Werther, and M. Hibberling observed that no precipitate of **thallic chloroplatinate** is formed when a thallic salt is added to hydrochloroplatinic acid.

S. Jolin,[30] J. C. G. de Marignac, and P. T. Cleve prepared **cerous chloroplatinate,** $CeCl_3.PtCl_4.13H_2O$, in quadratic, orange plates which are hygroscopic and lose 9 mols. of water at 110°. According to S. Jolin, and P. T. Cleve, the salt is very soluble in water, and alcohol. M. Holtzmann obtained deliquescent, orange prisms of $4CeCl_3.3PtCl_4.24H_2O$, which melt on the water-bath, and are soluble in water, and alcohol. P. T. Cleve, and J. C. G. de Marignac prepared **lanthanum chloroplatinate,** $LaCl_3.PtCl_4.13H_2O$, in orange, tabular crystals isomorphous with those of the cerium salt. The chloroplatinate is very soluble in water. F. T. Frerichs and E. F. Smith prepared a similar salt, $La_2(PtCl_6)_3.24H_2O$. C. von Scheele prepared **praseodymium chloroplatinate,** $PrCl_3.PtCl_4.12H_2O$, in yellow crystals of sp. gr. 2·412. J. C. G. de Marignac prepared the " didymium " salt. P. T. Cleve obtained **samarium chloroplatinate,** $SmCl_3.PtCl_4.10\frac{1}{2}H_2O$, in orange, deliquescent prisms of sp. gr. 2·712 ; C. Benedicks, **gadolinium chloroplatinate,** $GdCl_3.PtCl_4.10H_2O$, in orange-yellow prisms, of sp. gr. 2·719 ; L. F. Nilson, and P. T. Cleve, **yttrium chloroplatinate,** $4YCl_3.5PtCl_4.51$(or 52)H_2O, in red, deliquescent prisms, which melt at 100° with the loss of 10 mols. of water ; P. T. Cleve, **erbium chloroplatinate,** $ErCl_3.PtCl_4.10\frac{1}{2}H_2O$, in deliquescent plates which lose 3 mols. of water over sulphuric acid ; P. T. Cleve prepared **ytterbium chloroplatinate,** $2YbCl_3.PtCl_4.22H_2O$, in reddish-brown, deliquescent, rhombic plates, which effloresce in a desiccator, lose 11 mols. of water at 100° and melt below that temp. There is also a hydrate with 35 mols. of water. P. T. Cleve, **thorium chloroplatinate,** $ThCl_4PtCl_4.12H_2O$, in orange, deliquescent, tabular crystals, and L. F. Nilson, **zirconyl chloroplatinate,** $(ZrO)PtCl_6.12H_2O$, from a soln. of zirconyl chloride and hydrochloroplatinic acid, in pale yellow, four-sided prisms which melt below 100° with the loss of 6 mols. of water.

L. F. Nilson [31] obtained **stannic chloroplatinate,** $SnPtCl_8.12H_2O$, by evaporating to dryness on a water-bath a mixture of about 2 mols. of hydrochloroplatinic acid and 1 mol. of stannic chloride, extracting the mass with water, evaporating the soln. for crystallization, and drying the crystals between bibulous paper. The pale yellow plates do not change in dry air, but deliquesce in moist air ; they lose 2 mols. of water at 100°. K. Birnbaum, H. Töpsöe, and P. Rohland prepared **lead chloroplatinate,** $PbPtCl_6.3$(or 4)H_2O, by evaporating soln. of the theoretical proportions of the constituent chlorides. The pale yellow or orange-red, cubic crystals were found by H. Töpsöe to have a sp. gr. of 3·681, and a mol. vol. of 182·4. The crystals are stable in air, and they effloresce over sulphuric acid. According to H. Töpsöe, the crystals lose all their water at 125°, but W. Peters found that some water is retained at 200°. K. Birnbaum found that the salt is soluble in water, and in alcohol, and H. Töpsöe, and W. Peters observed that the salt in aq. soln. partially decomposes, forming sparingly soluble lead chloride and soluble platinic chloride.

L. F. Nilson [32] prepared **chromic chloroplatinate,** $CrCl_3.PtCl_4.10H_2O$, by evaporating on a water-bath a soln. of equimolar proportions of hydrochloroplatinic acid and green chromic chloride, extracting the dry mass with water, evaporating the soln. over sulphuric acid, and drying the crystals between bibulous paper. G. O. Higley washed the crystals with acetone, and dried them on a porous tile over sulphuric acid. The dark green, thin rhombic plates effloresce slowly in dry air ; they lose all but 10 mols. of water at 100°. They are freely soluble in water and in alcohol, but almost insoluble in acetone. G. O. Higley treated a soln. of the salt with silver nitrate and obtained silver chloroplatinate with a trace of silver chloride, and he inferred that the salt is a complex with doubled water molecules, $[Cr(H_4O_2)_5Cl]PtCl_6$. P. T. Cleve prepared **chromic chloroaquo-**

tetramminochloroplatinate, $[Cr(NH_3)_4(H_2O)Cl]PtCl_6$, in brownish-red, rhombic crystals by treating a soln. of chromic chloroaquotetramminochloride with hydrochloroplatinic acid. S. M. Jörgensen prepared **chromic chloropentamminochloroplatinate,** $[Cr(NH_3)_5Cl]PtCl_6$, in yellowish-brown rectangular prisms, by treating a soln. of chromic chloropentamminochloride with hydrochloroplatinic acid; and **chromic hexamminochloroplatinate,** $[Cr(NH_3)_6]Cl.PtCl_6.2\frac{1}{2}H_2O$, as yellow needles by the action of hydrochloroplatinic acid on a soln. of the hexamminochloride. The salt loses all its water in 24 hrs. at 100°, and it is decomposed by cold water or dil. hydrochloric acid to form $[Cr(NH_3)_6]_2Cl_4.PtCl_6.2H_2O$, which forms dark orange, prismatic or rhombic crystals, which lose a mol. of water at 100°. If the hexamminochloride is treated with sodium chloroplatinate in aq. soln., orange-yellow, six-sided plates or prisms of $[Cr(NH_3)_6]_2(PtCl_6)_3.6H_2O$, are formed. The salt is almost insoluble in water, and loses all its combined water in 24 hrs. at 100°—*vide* chromates, **11**. 60, 15; and dichromates, **11**. 60, 16.

W. J. Sell prepared complex **chromic carbamidochloroplatinate,** $2CrCl_3.PtCl_4.12CO(NH_2)_2.2H_2O$; P. Pfeiffer and P. Koch, **chromic trans-dichloroquaterethylenediaminechloroplatinate,** $[Cr\,en_2Cl_2]_2(PtCl_6).12H_2O$; P. Pfeiffer and T. G. Lando, **chromic cis-dichloroquaterethylenediaminechloroplatinate,** $[Cr\,en_2Cl_2]_2(PtCl_6).12H_2O$; R. F. Weinland and P. Dinkelacker, **chromic hexacetatodihydroxychloroplatinate,** as a *tetrahydrate*, $2[Cr_3(OH)_2(C_2H_3O_2)_6]PtCl_6.4H_2O$; A. Werner, the *pentahydrate*; R. F. Weinland and co-workers, the *decahydrate*; R. F. Weinland and E. Büttner, **chromic hexacetatodihydroxytriamminochloroplatinate,** $2[Cr_3(OH)_2(NH_3)_3(C_2H_3O_2)_6]PtCl_6$; and R. F. Weinland and E. Gussmann, **chromic hexacetatodihydroxytrispyridinechloroplatinate,** $2[Cr_3(OH)_2(C_5H_5N)_3(C_2H_3O_2)_6]PtCl_6$.

P. A. von Bonsdorff [33] prepared **manganese chloroplatinate,** $MnPtCl_6.6H_2O$, by the spontaneous evaporation of a soln. of the constituent chlorides; and H. Töpsöe, by the same process, or by cooling a hot, sat. soln. The dark yellow or orange prisms of the *hexahydrate* were found by H. Töpsöe, and H. Töpsöe and C. Christiansen to be trigonal, and to have the axial ratio $a:c=1:0.5310$, and $\alpha=111°\ 47'$; the $(10\bar{1})$-cleavage is complete; the sp. gr. is 2·692, and the mol. vol., 213·0. E. Herlinger gave 212·1 for the mol. vol. If the soln. is crystallized below 20°, H. Töpsöe observed that the *dodecahydrate*, which appears in pale yellow trigonal crystals with the axial ratio $a:c=1:0.7073$, and $\alpha=106°\ 36'$; positive birefringence; sp. gr. 2·112, and mol. vol. 322·6. The dodecahydrate is stable in air at low temp., but effloresces at a higher temp. It loses 10 mols. of water at 100°. L. Pauling studied the crystals. W. Peters observed that the crystals are stable at ordinary temp., in air, but they effloresce at a higher temp. They lose water and become brown at 160°, and take up ammonia to form a basic manganese salt, $MnPt(OH)Cl_5$.

P. A. von Bonsdorff prepared **ferrous chloroplatinate,** $FePtCl_6.6H_2O$, by the spontaneous evaporation of a soln. of the component chlorides. L. Pauling studied the crystals. The dark yellow, or brownish-yellow crystals were found by H. Töpsöe to be trigonal, with the axial ratio $a:c=1:0.5144$, and $\alpha=112°\ 14'$; sp. gr. 2·714, and mol. vol. 211·3. E. Herlinger gave 210·7 for the mol. vol. The salt is deliquescent, and it is readily oxidized in air, or in aq. soln. L. F. Nilson prepared **ferric chloroplatinate,** $FeCl_3.PtCl_4.10\frac{1}{2}H_2O$, by evaporating to dryness, on a water-bath, a mixed soln. of 2 mols. of hydrochloroplatinic acid, and a mol. of ferric chloride, extracting the mass with water, evaporating the aq. soln. over sulphuric acid, and drying the crystals between bibulous paper. The yellowish-red, deliquescent, four-sided prisms give off 5 mols. of water at 100°. H. St. C. Deville and J. S. Stas observed that when a soln. of platinic chloride is poured into one of ferric chloride with a great excess of ammonium chloride, ammonium chloroplatinate is precipitated, together with a yellow or brownish-yellow precipitate containing both iron and platinum.

P. A. von Bonsdorff [34] prepared **cobaltous chloroplatinate,** $CoPtCl_6.6H_2O$, by the spontaneous evaporation of soln. of the component salts. The brownish-yellow, or yellowish-brown deliquescent prisms of the *hexahydrate* were found by

H. Töpsöe, and H. Töpsöe and C. Christiansen to be trigonal with the axial ratio $a : c = 1 : 0.5140$, and $\alpha = 112° 14'$; the $(10\bar{1})$-cleavage is complete; and the birefringence positive. S. M. Jörgensen gave 2·699 for the sp. gr. L. Pauling studied the crystals. E. Herlinger gave 213·0 for the mol. vol. W. Peters obtained the anhydrous salt by heating the hexahydrate to 170°. The olive-green powder takes up dry ammonia to form the **cobaltous dodecamminochloroplatinate,** $CoPtCl_6.12NH_3$, at 22°, and at −20°, to form **cobaltous octodecamminochloroplatinate,** $CoPtCl_6.18NH_3$; and in vacuo, **cobaltous decamminochloroplatinate,** $CoPtCl_6.10NH_3$.

J. B. Rogojsky, W. Gibbs and F. A. Genth, S. M. Jörgensen, A. G. Bergman, and F M. Jagor described **cobaltic bishexamminochloroplatinate,** $[Co(NH_3)_6]_2(PtCl_6)_3.6H_2O$; S. M. Jörgensen, and F. Ephraim and W. Flügel, **cobaltic hexamminochloroplatinate,** $[Co(NH_3)_6]Cl(PtCl_6).\frac{1}{2}H_2O$; S. M. Jörgensen, $[Co(NH_3)_6]_2Cl_4(PtCl_6).2H_2O$; S. M. Jörgensen, **cobaltic trisethylenediaminechloroplatinate,** $[Co\,en_3]_2(PtCl_6)_3.12H_2O$; W. Gibbs and F. A. Genth, W. Gibbs, C. D. Braun, and S. M. Jörgensen, **cobaltic aquopentamminochloroplatinate,** $[Co(NH)_5(H_2O)]_2(PtCl_6)_3.6H_2O$; S. M. Jörgensen, $[Co(NH_3)_5(H_2O)]Cl(PtCl_6).\frac{1}{2}H_2O$, and $[Co(NH_3)_5(H_2O)]_2Cl_4(PtCl_6).2H_2O$; A. Werner, **cobaltic aquobisethylenediamineamminochloroplatinate,** $[Co(NH_3)\,en_2(H_2O)]_2(PtCl_6)_3.2H_2O$; S. M. Jörgensen, and A. Werner and A. Miolati, **cobaltic triaquotriamminochloroplatinate,** $[Co(NH_3)_3(H_2O)_3]_2(PtCl_6)_3.4H_2O$; F. Claudet, W. Gibbs and F. A. Genth, S. M. Jörgensen, and J. N. Brönsted and A. Petersen, **cobaltic chloropentamminochloroplatinate,** $[Co(NH_3)_5Cl]PtCl_6$; S. M. Jörgensen, **cobaltic chlorobisethylenediamineamminochloroplatinate,** $[Co(NH_3)\,en_2Cl]PtCl_6.H_2O$; S. M. Jörgensen, **cobaltic chloroaquotetramminochloroplatinate,** $[Co(NH_3)_4(H_2O)Cl]PtCl_6.2H_2O$; A. Werner and A. Klein, and G. Vortmann, **cobaltic dichlorotetramminochloroplatinate,** $[Co(NH_3)_4Cl_2]_2PtCl_4$; S. M. Jorgenson, **cobaltic dinitritotetramminochloroplatinate,** $[Co(NH_3)_4(NO_2)_2]_2PtCl_6$; A. Werner and R. Feenstra, **cobaltic dichloroquaterpyridinechloroplatinate,** $[Co\,py_4Cl_2]_2PtCl_6$; A. Werner and R. Frolich, **cobaltic dichlorobispropylenediaminechloroplatinate,** $[Co\,pn_2Cl_2]_2PtCl_6$; A. Werner and G. Lindenberg, **cobaltic dichlorobistrimethylenediaminechloroplatinate,** $[Co\,tn_2Cl_2]PtCl_6$; G. Vortmann, **cobaltic μ-peroxodecamminochloroplatinate,** $[Co_2(O_2)(NH_3)_{10}]Cl(PtCl_6)_2.5H_2O$; A. Werner and E. Kindscher, **cobaltic diol-octamminochloroplatinate,** $[Co_2(OH)_2(NH_3)_8](PtCl_6)_2.6H_2O$; A. Werner and co-workers, **cobaltic μ-amino-peroxo-quaterethylenediaminechloroplatinate,** $[Co_2(O_2,NH_2)\,en_4](PtCl_6)_2.3H_2O$; A. Werner and J. Fürstenberg, **cobaltic μ-acetato-amino-ol-hexamminochloroplatinate,** $[Co_2(C_2H_3O_2,NH_2,OH)(NH_3)_6]_2PtCl_6$; A. Werner and G. Jantsch, **cobaltic tetrol-diaquoquaterethylenediaminechloroplatinate,** $[Co_3(OH)_4\,en_4(H_2O)_2](PtCl_4)_2.2H_2O$; and S. M. Jörgensen, **cobaltic hexol-dodecamminochloroplatinate,** $[Co_4(OH)_6(NH_3)_{12}](PtCl_6)_3.2H_2O$—*vide supra.*

P. A. von Bonsdorff[35] prepared **nickel chloroplatinate,** $NiPtCl_6.6H_2O$, by spontaneously evaporating soln. of the component salts. The greenish-yellow prisms of the *hexahydrate* were found by H. Töpsöe to be trigonal, with the axial ratio $a : c = 1 : 0.5162$, and $\alpha = 112° 12'$; the $(10\bar{1})$-cleavage is complete; the birefringence is positive; W. Biltz gave for the sp. gr. 2·798; and the mol. vol., 206·3. L. Pauling studied the crystals. E. Herlinger gave 205·4 for the mol. vol. W. Peters found that the hexahydrate becomes anhydrous at 200°; and the brown product takes up dry ammonia to form **nickel dodecamminochloroplatinate,** $NiPtCl_6.12NH_3$, which in vacuo furnishes **nickel decamminochloroplatinate,** $NiPtCl_6.10NH_3$. N. S. Kurnakoff prepared **nickel bisethylenediaminechloroplatinate,** $NiPtCl_6.2C_2H_4(NH_2)_2$, and **nickel trisethylenediaminechloroplatinate,** $NiPtCl_6.3C_2H_4(NH_2)_2$.

Platinic oxychlorides.—According to M. Blondel,[36] platinic hydroxide dissolves in dil. hydrochloric acid, forming a soln. of the normal chloride, and when the sat. soln. is dialyzed, there is formed a product which coagulates when gently warmed, or mixed with a trace of an alkali salt. The coagulate is reddish-brown **platinic metoxyhydrochloride,** $(PtO_2)_5.2HCl.9H_2O$. It can be heated to 180° without losing hydrogen chloride, but it begins to decompose at 200°, forming platinous chloride. It is not soluble in water, but boiling water converts it into metaplatinic acid, $(PtO_2.H_2O)_5$. It dissolves slowly in hydrochloric acid to form both hydrochloroplatinous and hydrochloroplatinic acids.

L. N. Vauquelin noted that when hydrochloroplatinic acid is mixed with insufficient soda-lye to give it an alkaline reaction, and allowed to evaporate spontaneously, brownish-yellow, or grey laminæ are formed of a *sodium oxychloroplatinate,* of unknown composition.

M. Blondel also obtained an oxychloroplatinate by adding sodium hydroxide to a dil. soln. of sodium chloroplatinate at 100° so that the soln. remains acidic. In this way, 5 mols. of sodium hydroxide can be added per mol. of hydrochloroplatinic acid without reversing the acidity of the liquid. After dialysis, a product is formed with variable proportions of platinum, sodium, and chlorine. E. Johannsen obtained various *calcium oxychloroplatinates* by the action of calcium hydroxide on soln. of hydrochloroplatinic acid; and F. Weiss and F. Döbereiner, and E. Johannsen, various *barium oxychloroplatinates* by the action of barium hydroxide on that acid.

S. M. Jörgensen obtained some chromic hydroxychloroplatinates: **chromic hydroxydecamminochloroplatinate**, $[Cr_2(OH)(NH_3)_{10}]_2(PtCl_6)_5.10H_2O$, and $[Cr_2(OH)(NH_3)_{10}]_2Cl_4(PtCl_6)_3$; **chromic trihydroxyaquohexamminochloroplatinate**, $[Cr_2(OH)_3(NH_3)_6]_2(PtCl_6)_3.4H_2O$, and $[Cr_2(OH)_3(H_2O)(NH_2)_6]Cl(PtCl_3).H_2O$; G. Vortmann and O. Blasberg, **cobaltic hydroxychloroocatamminochloroplatinate**, $2Co(OH)Cl_2.PtCl_4.8NH_3.H_2O$; F. A. Genth, **ammonium cobaltic hydroxytriamminochloroplatinate**, $3NH_4Cl.Co_2(OH)_3Cl_3.2PtCl_4.3NH_3$; and G. Vortmann, $3NH_4Cl.2Co(OH)_2Cl.2PtCl_4.7NH_4.3H_2O$—*vide infra.*

Hydroxychloroplatinic acids.—A series of acids has been reported with the general formula $H_2PtCl_{6-n}(OH)_n$. A. Miolati and I. Bellucci, and I. Bellucci prepared **pentahydroxychloroplatinic acid,** $H_2Pt(OH)_5Cl$, by the action of cold $0{\cdot}1N$-H_2SO_4 on the corresponding barium salt. The brown, deliquescent syrup is a dibasic acid; it reacts with carbonates, slowly in the cold, rapidly when warmed. S. M. Jörgensen reported the corresponding anhydride **dioxyhydroxychloroplatinic acid,** $H_2PtO_2(OH)Cl$, to be probably formed when an aq. soln. of equimolar parts of platinic chloride and ammonia is evaporated to dryness, extracted with water, the filtered soln. treated with another molar part of ammonia, and then evaporated on the water-bath.

I. Bellucci, and A. Miolati and I. Bellucci prepared **silver pentahydroxychloroplatinate,** $Ag_2Pt(OH)_5Cl$, in brown flakes, by adding an excess of silver acetate to a soln. of the corresponding barium salt, and drying the washed precipitate over calcium chloride. E. Johannsen, and J. F. W. Herschel prepared **calcium pentahydroxychloroplatinate,** $CaPt(OH)_5Cl.H_2O$, by mixing hydrochloroplatinic acid with an excess of lime water in sunlight or violet light. The mixture remains clear in darkness. E. Johannsen, and A. Miolati and I. Bellucci used a somewhat similar process. A. Miolati, I. Bellucci, A. Miolati and I. Bellucci, and P. Klason discussed the nature of this salt. The white or yellowish-white powder can be obtained as tabular crystals. J. W. Döbereiner observed that at a red-heat, the salt loses 25 per cent. of water and oxygen to form a residue of calcium oxide and chloride, and platinous oxide. The salt is insoluble in water; soluble in hydrochloric and nitric acids; silver nitrate precipitates from the acidic soln. an orange-yellow precipitate; the nitric acid soln. with ammonium chloride was found by F. Weiss and F. Döbereiner slowly to form a precipitate of ammonium chloroplatinate. E. Johannsen observed that the salt is slowly decomposed in the presence of water and carbon dioxide. I. Bellucci, and A. Miolati and I. Bellucci prepared **strontium pentahydroxychloroplatinate,** $SrPt(OH)_5Cl.H_2O$, by a process analogous to that used for the calcium salt. A. Miolati also obtained **barium pentahydroxychloroplatinate,** $BaPt(OH)_5Cl.nH_2O$. E. Johannsen also prepared this salt; and A. Miolati and I. Bellucci obtained the *monohydrate.* I. Bellucci, and A. Miolati and I. Bellucci prepared **mercuric pentahydroxychloroplatinate,** $HgPt(OH)_5Cl$, by treating an acetic acid soln. of the barium salt with mercuric acetate; and similarly with **thallous pentahydroxychloroplatinate,** $TlPt(OH)_5Cl$; but with lead acetate a basic **lead pentahydroxychloroplatinate,** $Pb(OH)_2.PbPt(OH)_5Cl$, is formed.

A. Rosenheim and W. Löwenstamm obtained pale yellow **dihydroxytetrachloroplatinic acid,** $H_2Pt(OH)_2Cl_4.3H_2O$, or *oxytetrachloroplatinic acid,* $H_2PtOCl_4.4H_2O$, by allowing a soln. of platinic chloride to stand exposed to the atm. for some time. The acid was obtained by S. M. Jörgensen, W. Pullinger, and S. A. Norton by the action of hot water on silver chloroplatinate. The soln. is evaporated and heated to 100° when H_2PtOCl_4 is formed, but a further dehydration cannot be effected without decomposing the compound. The aq. soln. has an acidic reaction, and

readily decomposes carbonates. It behaves like a dibasic acid, forming a series of salts. M. Boll studied the hydrolysis of the acid in light.

A. Miolati prepared a soln. of **sodium dihydroxytetrachloroplatinic acid** by mixing soln. of platinic chloride with sodium hydroxide in theoretical proportions. The mol. conductivity of a soln. of a mol in v litres is :

v . . .	32	64	128	256	512	1024
μ . . .	86·4	90·2	93·3	97·03	103·4	105·8

and $\mu_{1024}-\mu_{32}=19·4$, corresponding with the regular value for a dibasic acid. A. Miolati prepared **copper dihydroxytetrachloroplatinic acid,** $CuPt(OH)_2Cl_4$, by the action of a soln. of platinic chloride on freshly-precipitated cupric hydroxide in excess, evaporating the filtered liquor in vacuo over sulphuric acid, dissolving the gum-like mass in absolute alcohol, adding dry ether, and evaporating the filtered liquor in vacuo over phosphorus pentoxide. S. M. Jörgensen obtained **silver dihydroxytetrachloroplatinate,** $Ag_2Pt(OH)_2Cl_4$, by treating a cold soln. of platinic chloride with silver nitrate, and drying the washed precipitate at 100°. The salt was also discussed by F. Reiff, A. Miolati, W. Hittorf and H. Salkowsky, and I. Jacobsen. The yellowish-brown, amorphous salt is decomposed by boiling water to form the tetrahydroxydichloroplatinate, and hydrochloric acid converts it into silver chloride and hydrochloroplatinic acid. A. Miolati prepared **zinc dihydroxytetrachloroplatinate,** $ZnPt(OH)_2Cl_4.3H_2O$, as in the case of the copper salt. The yellowish-brown product is freely soluble in water and in alcohol. The corresponding **cadmium dihydroxytetrachloroplatinate,** $CdPt(OH)_2Cl_4$, was also prepared ; and likewise **thallous dihydroxytetrachloroplatinate,** $Tl_2Pt(OH)_2Cl_4$, as a yellowish-brown powder ; insoluble in water, decomposed when allowed to stand over sulphuric acid ; and not changed by a prolonged digestion with a soln. of thallous sulphate on a water-bath. The corresponding **lead dihydroxytetrachloroplatinate,** $PbPt(OH)_2Cl_4$, was prepared, and it appears to be associated with more or less basic salt, $Pb(OH)_2.PbPt(OH_2)Cl_4$.

I. Jacobsen prepared **tetrahydroxydichloroplatinic acid,** $H_2Pt(OH)_4Cl_2$, in aq. soln. by the action of silver nitrate on a cold soln. of hydrochloroplatinic acid in the molar proportions 2 : 1, washing the precipitate with ice-water, and treating the product with hot water on a water-bath. The resulting dihydroxytetrachloroplatinic acid is treated with 2 mols. of silver nitrate, and the precipitate is washed and boiled for about 8 hrs. M. Blondel obtained it by treating platinic oxide, $PtO_2.4H_2O$, at 0° with dil. hydrochloric acid (1 : 5), and separating the soln. from the undissolved platinic oxide. A. Miolati and U. Pendini prepared the salt by mixing equimolar parts of $0·1N$-HCl and hydrochloroplatinic acid in the cold, evaporating the soln. to dryness, and extracting the dry mass with water. Ammonium chloroplatinate remains undissolved, and the filtered soln. can be again evaporated and the treatment repeated two or three times. A black, hygroscopic mass of tetrahydroxychloroplatinic acid is thus obtained. M. Blondel observed that the solid is unstable even at 0°, and rapidly changes to hydrochloroplatinic acid, and when the acid soln. is diluted with water hydrated platinic dioxide, $PtO_2.4H_2O$, is precipitated. I. Jacobsen found that the soln. is darkened by an excess of aq. ammonia, and after a time, a brown precipitate is formed. The reaction proceeds more quickly with hot soln. M. Blondel showed that potassium chloride does not give a precipitate of K_2PtCl_6 when added to the aq. soln. ; and other alkali salts furnish a gelatinous precipitate which is soluble in much water. S. M. Jörgensen reported **dioxydichloroplatinic acid,** $H_2PtO_2Cl_2$, to be formed as a brownish-black, amorphous, deliquescent mass by evaporating a mixed soln. of equimolar parts of ammonia and of $PtCl_4.5H_2O$, extracting the dry mass with water, evaporating the aq. soln. on a water-bath, and drying the product at 100°.

A. Miolati and U. Pendini prepared **silver tetrahydroxydichloroplatinate,** $Ag_2Pt(OH)_4Cl_2$, as a dark brown precipitate, by adding a sat. soln. of silver acetate

to a cold, conc. soln. of the corresponding acid. They also obtained **mercuric tetrahydroxydichloroplatinate,** $HgPt(OH)_4Cl_2$, by adding mercuric acetate to a soln. of the acid. The yellowish-red precipitate is soluble in hydrochloric acid; and impure **thallous tetrahydroxydichloroplatinate,** $Tl_2Pt(OH)_4Cl_2$, was prepared. The corresponding **lead tetrahydroxydichloroplatinate,** $PbPt(OH)_4Cl_2$, was obtained as a flocculent, reddish-yellow precipitate.

M. Blondel described a **silver platinum oxychloride,** $AgCl.4PtO_2.HCl.4H_2O$, to be formed by adding silver nitrate to a soln. of platinic oxide in hydrochloroplatinic acid. It is decomposed by warm water.

L. Pigeon reported a platinic hydropentachloride, $HCl.PtCl_4.2H_2O$, to be formed by heating hydrochloroplatinic acid, $H_2PtCl_6.6H_2O$, in vacuo, in the presence of potassium hydroxide, for 2 or 3 days on a water-bath—*vide supra*—but A. Miolati and I. Bellucci showed that the product is more likely to be **hydroxypentachloroplatinic acid,** $H_2Pt(OH)Cl_5.nH_2O$. It forms a reddish-brown, deliquescent mass which gives a pale yellow, acid, aqueous soln. readily decomposing carbonates in the cold. With ammonia soln., it gives no precipitate, and on heating the liquid it becomes almost colourless. Ammonium and potassium chlorides precipitate the respective platinichlorides. The mol. electrical conductivity of a soln. of a mol of the salt in v litres at 25°, is:

v . . .	32	64	128	256	512	1024
μ . . .	282·9	304·0	329·3	359·3	392·6	430·5

The change in the electrical conductivity is attributed to hydrolysis; and titration experiments with 0·1N-NaOH and phenolphthalein as indicator show that one of the two replaceable hydrogen atoms has a strongly acidic character, whilst the other has only weak acidic properties.

O. Ruff and W. Jeroch added a conc. soln. of potassium fluoride to platinic chloride, and dried the yellow, amorphous **potassium hydroxypentachloroplatinate,** $K_2Pt(OH)Cl_5$, on a porous tile. The salt is readily soluble in water. A. Miolati and I. Bellucci obtained **lithium hydroxypentachloroplatinate,** $Li_2Pt(OH)Cl_5$, in yellow needle-like crystals, by exactly neutralizing a soln. of the acid with lithium hydroxide, and allowing the soln. to stand in vacuo. They obtained a soln. of **sodium hydroxypentachloroplatinate,** $Na_2Pt(OH)Cl_5$, in a similar manner, and found the electrical conductivity of soln. of a mol of the salt in v litres to be:

v . . .	32	64	128	256	512	1024
μ . . .	93·2	97·5	101·3	104·5	109·4	117·0

so that $\mu_{1024}-\mu_{32}=23·8$, the regular value for the neutral sodium salt of a dibasic acid. A. Miolati and I. Bellucci could not prepare copper hydroxypentachloride. The corresponding **silver hydroxypentachloroplatinate,** $Ag_2Pt(OH)Cl_5$, was obtained as a yellow precipitate, stable in boiling water, by treating a cold soln. of the acid and with silver nitrate. A. Miolati and I. Bellucci prepared **strontium hydroxypentachloroplatinate,** $SrPt(OH)Cl_5.H_2O$; and also **barium hydroxypentachloroplatinate,** $BaPt(OH)Cl_5.4H_2O$, in orange-yellow prisms, by neutralizing a soln. of the acid with baryta water, and concentrating the soln. in a desiccator; but **zinc hydroxypentachloroplatinate,** $ZnPt(OH)Cl_5$, could not be prepared; but the corresponding **cadmium hydroxypentachloroplatinate,** $CdPt(OH)Cl_5$, was obtained in an impure state. Rose-red **thallous hydroxypentachloroplatinate,** $Tl_2Pt(OH)Cl_5$, was obtained by mixing soln. of the corresponding acid with thallous acetate; with lead acetate a basic **lead hydroxypentachloroplatinate,** $Pb(OH)_2.PbPt(OH)Cl_5$, was formed.

P. T. Cleve prepared **platinic trichloronitritodiammine,** $[Pt(NH_3)_2Cl_3(NO_2)]$; **platinic trans-dichlorodinitritodiammine,** $[Pt(NH_3)_2Cl_2(NO_2)_2]$, a complex salt with silver nitrate, **platinic cis-dichlorodinitritodiammine,** and also **platinic hydroxychlorodinitritodiammine,** $[Pt(NH_3)_2(OH)(NO_2)Cl]$; F. Reiff described the complex with **hydroxyaquotetrachloroplatinic acid,** $H[PtCl_5(H_2O)(OH)].C_4H_8O_2$.

According to J. L. Proust,[37] if a soln. of hydrochloroplatinic acid be decomposed by potash-lye, the precipitate of **fulminating platinum** detonates at an elevated temp., but not so vigorously as fulminating gold or silver. J. W. Döbereiner added that the straw-yellow precipitate of $3PtO_2.NH_3$ detonates feebly with rapid heating, and more vigorously with slow heating. A. F. de Fourcroy and L. N. Vauquelin made analogous observations; and E. Davy treated platinic sulphate with ammonia, boiled the precipitate with potash-lye, and dried the washed precipitate. The brown product is stable in air; it does not detonate by trituration, shock, or the electric spark, but it detonates vigorously when heated to 205°. Chlorine water converts it into ammonium chloride and hydrochloroplatinic acid; hydrochloric acid does not attack it perceptibly; sulphuric acid dissolves it, forming a dark brown liquid without the evolution of gas; and nitric acid converts it into a basic nitrate.

E. von Meyer applied the term *Knallplatine* or **fulminoplatinums** to a number of bodies obtained by the action of potash-lye on ammonium chloroplatinate. These bodies are nearly insoluble in water, and do not form definite compounds with either acids or alkalies. The nitrogen contained in them is so firmly held in combination that they give off no ammonia when boiled with strong potash solution. When heated *per se* they undergo total decomposition, generally with explosive violence, owing to the sudden liberation of a large quantity of nitrogen. When ammonium chloroplatinate is boiled with a quantity of aqueous potash insufficient for complete decomposition, added very slowly, a product of the formula $PtNClO_3H_6$ is obtained, the formation of which may be represented by the equation: $(NH_4)_2PtCl_6+5KOH=5KCl+2H_2O+NH_3+PtNClO_3H_6$. The chemical behaviour of this body, and the existence of other bodies standing in simple relations to it, show, however, that the formula here indicated must be quadrupled so as to make $Pt_4N_4Cl_4O_{12}H_{24}$—or platinum fulminotetrachloride. Its relation to the other three fulminoplatinums is indicated by the following equations: $Pt_4N_4Cl_4O_{12}H_{24}+KOH=KCl+Pt_4N_4Cl_3(OH)O_{12}H_{24}$ (fulminotrichloride); $Pt_4N_4Cl_4O_{12}H_{24}+2KOH=2KCl+2H_2O+Pt_4N_4Cl_2O_{12}H_{22}$ (fulminodichloride); and $Pt_4N_4Cl_4O_{12}H_{24}+3KOH=3KCl+2H_2O+Pt_4N_4Cl(OH)O_{12}H_{22}$ (fulminomonochloride). According to E. von Meyer, the decomposition of ammonium chloroplatinate by potash-lye results in the formation of bodies containing equal numbers of atoms of platinum and nitrogen, whence it follows that ammonium chloroplatinate cannot be regarded as a double salt of platinic chloride and ammonium chloride, $PtCl_4(NH_4Cl)_2$, the two atoms of nitrogen having essentially different functions in the compound. When ammonium chloroplatinate is heated even with a large excess of potash, only half the nitrogen is eliminated in the form of ammonia. The constitution of these four substances has not been determined.

The first member of the series, **platinum fulminotetrachloride,** $Pt_4N_4Cl_4O_{12}H_{24}$, is obtained only with great difficulty, one of its atoms of chlorine being very easily eliminated. It is formed by heating ammonium chloroplatinate with aq. potash-lye (4·6 mols.), added very slowly until a temporary alkaline reaction is produced. The pale yellow precipitate is purified by repeated boiling with very dil. acetic acid and water. A slight excess of potash-lye determines the formation of bodies containing less chlorine. Platinum fulminotetrachloride when digested with aq. ammonia gives up half its chlorine, and when evaporated with ammonia over the water-bath, it loses three-fourths of its chlorine; whence it appears that two atoms of chlorine are eliminated easily, and a third with more difficulty, whilst the fourth is firmly held in combination. The bodies formed by the action of ammonia explode violently when heated. When gently heated with oxalic acid in presence of dil. sulphuric acid, platinum fulminotetrachloride gives off a quantity of carbon dioxide corresponding to a loss of 3 atoms of oxygen from each mol. At 150° it gives off 4 mols. of water.

The second member of the series, **platinum fulminotrichloride,** $Pt_4N_4Cl_3(OH)$-$O_{12}H_{24}$, is formed when ammonium chloroplatinate is decomposed with an

insufficient quantity of potash-lye (4·5 to 5 mols.), added in small portions somewhat rapidly. At 150°, it loses 3 mols. of water, and when more strongly heated, it explodes, giving off gases which consist mainly of nitrogen but contain also free oxygen. When treated with ammonia, it gives up two atoms of chlorine. It is acted on by oxalic acid in the same manner as the tetrachloride, the carbon dioxide evolved corresponding with a loss of 3 atoms of oxygen from each molecule. After the reaction the liquid contains a black precipitate, which gives off ammonia when heated with soda. When gently heated in hydrogen, the trichloro-compound undergoes violent decomposition, yielding water, ammonia, and free nitrogen.

The third member of the series **platinum fulminodichloride,** $Pt_4N_4Cl_2O_{12}H_{22}$, is formed on heating ammonium chloroplatinate with aq. potash-lye, added in moderate quantities until the liquid remains slightly alkaline and ceases to evolve ammonia. It is a fine yellow body, closely resembling the compound last described in most of its reactions. It is completely decomposed by treatment with zinc and sulphuric acid, the platinum being thrown down in a finely-divided metallic state, whilst the whole of the chlorine goes into solution. Sulphur dioxide passes into water in which the compound is suspended, gradually dissolves it, forming a nearly colourless solution, which when neutralized with sodium carbonate and evaporated yields crystals of the salt, $2PtSO_3.6Na_2SO_3.3H_2O$.

The fourth member of the series, **platinum fulminochloride,** $Pt_4N_4Cl(OH)O_{12}H_{22}$, is obtained as a dark yellow powder by heating ammonium chloroplatinate with 4·7 mols. of potash-lye added at once, until ammonia is no longer evolved. It loses 4 mols. of water at 152°. When gradually heated to 260° with sodium carbonate, nearly the whole of the hydrogen is oxidized to water, whilst the nitrogen is for the most part set free. It is not appreciably acted on by oxalic acid. With nascent hydrogen, it behaves like the dichloro-compound—*vide supra.*

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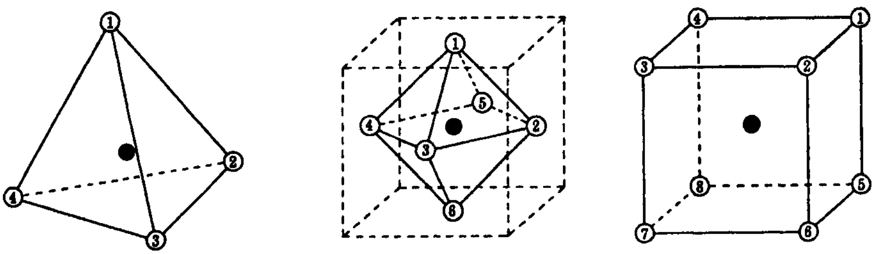
§ 23. The Platinum Ammines

The platinum ammines are here arranged as in the analogous cases of the chromic and cobaltic ammines. There is a long list in the *Platiake* of W. Loewenstein in L. Gmelin and K. Kraut, *Handbuch der anorganischen Chemie* (Heidelberg, **5**. iii, 429, 1915). F. Reitzenstein,[1] and I. I. Tscherniaeff studied the complex salts. For the complexes with platinum monochloride, *vide supra.*

The mechanism of the linkage of the co-ordinated molecules with the central atom of the nucleus has not been fully explained. In one version of the electronic theory, the linkage is attributed to the transfer of a pair of electrons by each co-ordinated molecule as donor. This furnishes an outer ring or shell of electrons exceeding the stable octet. Rings or shells with 12 and 18 electrons are assumed to form stable rings or shells in complexes in which the co-ordination number is 6 or 8. To overcome the difficulty, some of the linkages formed by the electrons are assumed to be singlets ; or else they are attributed to dipole valency, thus, in a compound of the type $[M(NH_3)_m]X_n$, the negative charge on the electrons will be greatest at the corners of the usual octet, and weakest at the centres of the faces of the corresponding cube since the positive charge of the central atom will there be greatest. In other words, the central atom will be surrounded by an electric field with six positive poles corresponding with the faces of the cube—Fig. 87.



FIGS. 87 to 89.—Arrangement for Molecules with Co-ordination Numbers, 4, 6, and 8.

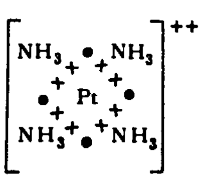
Consequently, when the central atom is approached by a dipole molecule, like water or ammonia, the negative portion—oxygen or nitrogen as the case may be—is attached to one of the six mid-points of the faces of the cube—dotted in Fig. 88—so that the six molecules will be arranged about the central atom at the corners of a regular octahedron. As previously indicated, P. Stoll (1926), and R. W. G. Wyckoff (1931), have shown that in the crystal lattices of compounds like $K_2[PtCl_6]$, $Rb_2[PdBr_6]$, $[Ni(NH_3)_6]Cl_2$, $[Co(NH_3)_6]I_3$, and $(NH_4)_2[SiF_6]$, the ammonia molecules or the halogen atoms in the square brackets are arranged at the corners of an octahedron surrounding the central atom. This shows the origin of the co-ordination number 6. In this co-ordination, the "neutral" molecules are attached by the negative portions to the positive surface of the central atom. The electrical field is concentrated in the "neutral" molecules so that the electronegative X-atoms

are forced away from the central atom, and exhibit ionization: $[M(NH_3)_m]X_n = [M(NH_3)_m]^{\cdot} + nX'$. The co-ordination number is 4 when the 4 molecules are arranged about the central atom at the corners of a regular tetrahedron—Fig. 87; and the co-ordination number is 8 when the 8 molecules are arranged about the central atom at the corner of a cube—Fig. 89. When the six co-ordinated molecules completely surround the central atom so that there is no space available for the introduction of more molecules, the co-ordination number 6 cannot be exceeded. Suppose each face of the cube—Fig. 88—could accommodate two molecules, the co-ordination number would rise to 12.

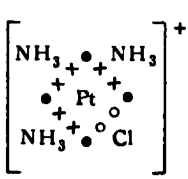
The presence of electrical fields about atoms and molecules does not mean that all are capable of dipole attachment without electronic exchange. The fields may be too feeble, or vibrational energy of the molecules due to heat may prevent the formation of these compounds by dipole valency. The effect of the positive charge in favouring this kind of union is more marked when it lies near to the atomic nucleus, such as occurs when the atoms are small; and with a given metal, it is greater, when the metal is exercising its higher valencies.

Molecules like NH_3 and H_2O act as dipoles, and they are attached to the central atom covalently by electrostatic attraction, but charged ions may also attach themselves also by electrostatic attraction. Thus, in ferric chloride, $FeCl_3$, the octets about the four atoms are completed electrovalently. The octet of iron has positive charges located at the centres of six faces of the imaginary (dotted) cube, Fig. 88, and here are attached electrostatically three Cl′-ions. The remaining three positive charges attract the negative ions of three molecules of cæsium chloride. There are therefore six chlorine ions, respectively, at the six apices of the octahedron, Fig. 88. The neutral molecules, CsCl, are attached to the positive surface of the central atom by negative ions, and the oppositely-charged ions remain in the outer sphere so that, on ionization, $Cs_3[FeCl_6] \rightleftharpoons 3Cs^{\cdot} + [FeCl_6]'''$. The chlorine ions in such complexes, $[MCl_6]'''$, are not liberated as single ions unless the complex is decomposed, but are held tenaciously by dipole valency to the apices of the octahedron, Fig. 89. If one of these positions is taken up by a molecule of water, ammonia, or some other neutral body, a Cl′-ion is released. The electrical nature of the combination is not apparent before the displacement has taken place; no charge is acquired by the chlorine ion in separating from the complex, because it was already charged in the complex itself.

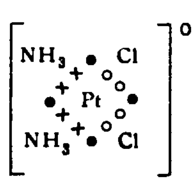
According to the electronic theory of valency, in the platinous ammines, starting with the central platinous, : Pt :, with a group of four valency electrons, the tetrammine is formed by the introduction of four ammonia molecules, in which each molecule shares a pair of electrons with the platinum atom by means of a duplet linkage. This raises the number of electrons in the ring to twelve, so that there is a stable dodecet instead of an octet grouping—*vide supra*, singlet linkages. If one of the ammonia molecules be replaced by, say, a neutral chlorine atom, the ammonia molecule taking away with it two shared electrons, and the chlorine atom bringing in only one electron, means that there is an electron short. This is made good by the complex bringing in an electron from outside, thus reducing the positive charge of the nucleus by one unit. In that way, $[Pt(NH_3)_4]^{++}$ passes into $[Pt(NH_3)_3Cl]^{+}$, and so on with successive replacements of NH_3-groups by Cl-atoms, until, at the limit, a chloroplatinite, $[PtCl_4]^{--}$, say potassium chloroplatinite, $K_2[PtCl_4]$:



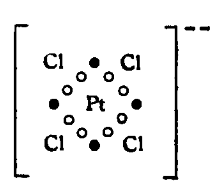
$[Pt(NH_3)_4]^{\cdot\cdot}$-ion



$[Pt(NH_3)_3Cl]^{\cdot}$-ion

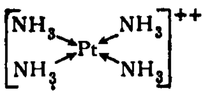


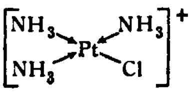
$[Pt(NH_3)_2Cl_2]$

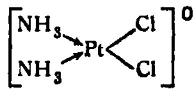


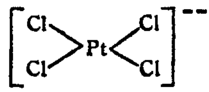
$[PtCl_4]''$-ion

where ● denotes the electrons of platinum; ○, those of chlorine; and $_+$, those of ammonia is formed. One of the two chlorine electrons comes out of the nucleus, and this reduces the positive charge of the nucleus by one unit for each chlorine electron brought in from outside. Since the symbol → is used to indicate a valency bond in which two shared electrons are supplied by one atom, or atomic group, as donor, and the symbol — for an ordinary valency bond formed by two atoms sharing a pair of electrons, the alternative symbols for the platinous compounds are of the type:

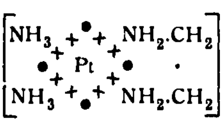

Tetrammino-


Chlorotriammino-

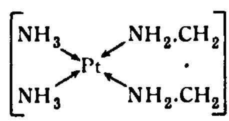

Dichlorodiammino-


Tetrachloroplatinite

In the ammines, ammonia can be replaced, molecule by molecule, by pyridine, C_5H_5N, methylamine, $CH_3.NH_2$, etc. In these compounds, each nitrogen atom shares a pair of electrons with the central atom of, say, platinum; but with a molecule of ethylenediamine, $NH_2.CH_2.CH_2.NH_2$—often written *en*, for the sake of brevity—each of the two nitrogen atoms of ethylenediamine can contribute a pair of electrons to the central atom to form what G. T. Morgan (1920) called *chelate compounds*—from χηλή, a claw—in allusion to the pincer-like claws of the crustacea; thus:

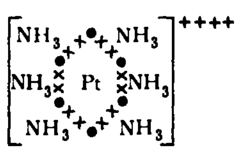


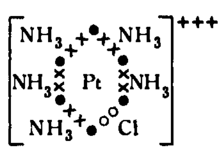
or

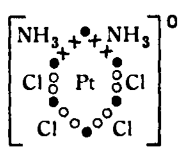


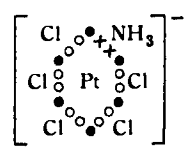
$Pt(NH_3)_2(NH_2\ CH_2\ CH_2.NH_2)]$ or $[Pt(NH_3)_2\ en]$

In the platinic ammines, the central platinic atom, : P̈t :, with an uncompleted group of six electrons, in forming the hexammine, takes up six ammonia molecules by double linkages, and this makes a total of 18 electrons. If one of the ammonia groups is replaced by chlorine, which donates only one electron to the central platinum atom, another electron must come from outside to complete the octodecet grouping. This reduces the original charge of four positive units to three:


$[Pt(NH_3)_6]^{\cdot\cdot\cdot\cdot}$-ion


$[Pt(NH_3)_5Cl]^{\cdot\cdot\cdot}$-ion


$[Pt(NH_3)_2Cl_4]$


$[Pt(NH_3)Cl]'$-ion

When a univalent, electronegative radicle like chlorine displaces a molecule of ammonia, or water, the positive valency of the complex drops by one unit for each substitution until the neutral ammine is attained. Beyond that, the introduction of another electronegative radicle in place of ammonia, renders necessary the introduction of an extra electron from outside, and this imparts a negative charge to the complex $Pt(NH_3)Cl_5$-ion. At the limit, there is formed the complex, bivalent, electronegative $PtCl_6{}''$-ion, typified by the salt, potassium chloroplatinate, K_2PtCl_6. These remarks apply, *mutatis mutandis*, also to other ammines—*e.g.* cobalt, chromium, iridium, and many other metals.

It will be observed that in the electronic theory, A. Werner's distinction between principal and subsidiary valencies is virtually superseded, and, as pointed out by N. V. Sidgwick (1927), *according to the electronic theory, all the valencies attaching the groups to the central atom are the same; otherwise expressed, the number of shared*

electrons in the valency group of the central atom is the same whether the co-ordinated units are molecules or univalent radicles; and, accordingly, the one kind can replace those of the other kind, unit by unit. The special feature of A. Werner's hypothesis still retained is the co-ordination number which represents the number of groups joined to the central atom by non-ionizable linkages whether these are linkages of univalent radicles, or whole molecules.

I.—*The platinous ammines with one platinum atom in the nucleus.*

1.—**The pentammine family,** or compounds of the bivalent basic group $[PtA_5]''$.

(i) *Trianilinodiammines,* $[Pt(NH_3)_2(C_6H_5NH_2)_3]X_2$, represented by the (1) chloride; and (2) sulphate.

(ii) *Ethylenesulphinotriammines,* $[Pt(NH_3)_3\{(C_2H_4)_2S_2\}]X_2$, represented by the (1) chloride; and (2) sulphate.

2.—**The tetrammine family,** or compounds of the bivalent basic group $[PtA_4]''$.

(i) *Tetrammines,* $[Pt(NH_3)_4]X_2$, represented by (1) hydroxide; (2) chloride—and double chlorides with those of copper, barium, zinc, mercury, tin, lead, cobalt, and platinum (ous and ic), and other double salts with ammonia, ethylamine, pyridine, ethylene, and amyl alcohol; (3) bromide and a bromoplatinite, and a complex with amyl alcohol; (4) iodide and a complex with mercury iodide; (5) sulphite, chlorosulphite, and sulphitoplatinites; (6) hydrosulphite and hydrosulphitoplatinites; (7) sulphate; (8) hydrosulphate; (9) nitrite, and nitritoplatinite; (10) nitrate, and nitratoplatinate; (11) phosphate and complexes with the ammonium phosphates; (12) carbonates; (13) hydrocarbonates; (14) acetate; (15) oxalate and oxalatoplatinite; (16) hydroxalates; (17) tartrate; (18) hydrotartrate; (19) picrate; (20) phenylmercaptide; (21) phenylthioglycolate; (22) thiocyanate and thiocyanatoplatinite; (23) ferrocyanide; (24) cyanoplatinite; (25) chromate; and (26) dichromate.

(ii) *Tetrahydrazines,* $[Pt(N_2H_4)_4]X_2$, represented by the (1) chloride; and (2) iodide.

(iii) *Dihydrazinodiammines,* $[Pt(NH_3)_2(N_2H_4)_2]X_2$, represented by the cis- and trans-chlorides, chloroplatinite, and chloropalladite.

(iv) *Tetrahydroxylamines,* $[Pt(NH_2OH)_4]X_2$, represented by (1) hydroxide; (2) chloride, basic chlorides, and chloroplatinite; (3) hydrochloride; (4) bromide; (5) sulphate; (6) nitrate; (7) phosphate; and (8) oxalate.

(v) *Trihydroxylaminoammines,* $[Pt(NH_3)(NH_2OH)_3]X_2$, represented by the chloride, and the chloroplatinite and chloropalladite.

(vi) *Hydroxylaminotriammines,* $[Pt(NH_3)_3(NH_2OH)]X_2$, represented by the chloride and chloroplatinite.

(vii) *Dihydroxylaminodiammines,* $[Pt(NH_3)_2(NH_2OH)_2]X_2$, represented by the chloride.

(viii) *Dihydroxylaminobispyridines,* $[Pt(NH_2OH)_2py_2]X_2$, represented by the chloride, and chloroplatinite.

(ix) *Aquotriammines,* $[Pt(NH_3)_3(H_2O)]X_2$, represented by the (1) chloroplatinite, and (2) bromoplatinite.

(x) *Quatermethylamines,* $[Pt(CH_3NH_2)_4]X_2$, represented by the chloride and chloroplatinite.

(xi) *Quaterethylamines,* $[Pt(C_2H_5NH_2)_4]X_2$, represented by the (1) chloride, some isomeric forms, chloroplatinite, and chloroamminoplatinates; (2) bromide; (3) sulphate; (4) nitrate; and (5) oxalate.

(xii) *Quaterpropylamines,* $[Pt(C_3H_7NH_2)_4]X_2$, represented by the chloride and the chloroplatinite.

(xiii) *Quaterbutylamines*, $[Pt(C_4H_9NH_2)_4]X_2$, represented by the chloride and the chloroplatinite of the normal and isobutylamines.

(xiv) *Quateramylamines*, $[Pt(C_5H_{11}NH_2)_4]X_2$, represented by the chloroplatinite.

(xv) *Quaterdimethylamines*, $[Pt\{(CH_3)_2NH\}_4]X_2$, represented by the chloride and chloroplatinite.

(xvi) *Quaterbenzylamines*, $[Pt(C_6H_5.CH_2.NH_2)_4]Cl_2$.

(xvii) *Quateranilines*, $[Pt(C_6H_5NH_2)_4]X_2$, represented by the chloride.

(xviii) *Bisethylenediamines*, $[Pt\,en_2]X_2$, represented by (1) chloride and its double salts with copper, cobalt, and platinous chlorides; (2) bromide and the double salts with copper and platinous bromides; (3) perchlorate; (4) carbonate; (5) oxalate; and (6) cyanoplatinate.

(xix) *Bispropylenediamines*, $[Pt\,pn_2]X_2$, represented by racemic, lævo-, and dextro-salts: by (1) hydroxide; (2) chloride; (3) bromide; (4) iodide; (5) sulphate; (6) nitrate; and (7) picrate.

(xx) *Quaterpyridines*, $[Pt\,py_4]X_2$, represented by (1) hydroxide; (2) chloride, the double salts with copper, zinc, cadmium, cobalt, platinous, and platinic chlorides, as well as by complexes with the ammino-, ethylamine-, and pyridine-trichloroplatinates; (3) bromide; (4) iodide; (5) sulphite; (6) sulphate and double sulphates with copper and zinc; (7) hydrosulphate; (8) dithionate; (9) nitrite and nitritoplatinite; (10) nitrate and bromonitrate; (11) hydronitrate; (12) carbonate; (13) hydrocarbonate; (14) thiocyanate; (15) acetate; (16) oxalate; (17) chromate; and (18) dichromate.

(xxi) *Quatermethylcarbylamines*, $[Pt(CH_3.NC)_4]X_2$, represented by the (1) chloroplatinite; and (2) picrate.

(xxii) *Quaterbutylcarbylamines*, $[Pt(C_4H_9.NC)_4]X_2$, represented by the (1) chloride and chloroplatinite; (2) cyanoplatinite; and (3) picrate.

(xxiii) *Quaterphenylcarbylamines*, $[Pt(C_6H_5.NC)_4]X_2$, represented by the (1) chloroplatinite; and (2) bromoplatinite.

(xxiv) *Quateraminoacetals*, $[Pt\{NH_2.CH(OC_2H_5)_2\}_4]X_2$, represented by the chloride and chloroplatinite.

(xxv) *Quaterthioacetamides*, $[Pt(CH_3.CS.NH_2)_4]X_2$, represented by (1) chloride and chloroplatinate; and (2) sulphate.

(xxvi) *Quaterthiocarbamides*, $[Pt\{CS(NH_2)_2\}_4]X_2$, represented by (1) chloride and chloroplatinate; (2) bromide; (3) iodide; (4) sulphate; (5) nitrate; (6) thiocyanate; and (7) picrate.

(xxvii) *Quatermethylthiocarbamide*, $[Pt\{CS(NH_2)(NHCH_3)\}_4]X_2$, represented by the chloride.

(xxviii) *Quaterethylthiocarbamide*, $[Pt\{CS(NH_2)(NHC_2H_5)\}_4]X_2$, represented by the chloride.

(xxix) *Quater-iso-undecylthiocarbamide*, $[Pt\{(CSNH_2)(NHC_{11}H_{23})\}_4]X_2$, represented by the chloride.

(xxx) *Quaterdiethylthiocarbamide*, $[Pt\{CS(NHC_2H_5)_2\}_4]X_2$, represented by the chloride.

(xxxi) *Quaterdi-iso-undecylthiocarbamide*, $[Pt\{CS(NHC_{11}H_{23})_2\}_4]X_2$, represented by the chloride.

(xxxii) *Quatertriethylthiocarbamide*, $[Pt\{CS(NHC_2H_5)(N(C_2H_5)_2)\}_4]X_2$, represented by the chloride.

(xxxiii) *Quaterxanthogenamides*, $[Pt(NH_2CS.OC_2H_5)_4]X_2$, represented by (1) chloride and chloroplatinate; and (2) sulphate.

(xxxiv) *Quatermethylsulphines*, $[Pt\{(CH_3)_2S\}_4]X_2$, represented by (1) chloride, chloroplatinite, and chloroplatinate; (2) bromoplatinite; (3) sul-

phate ; (4) nitritoplatinite ; (5) nitrate ; (6) picrate ; and (7) nitroprusside.

(xxxv) *Quaterethylsulphines*, $[Pt\{(C_2H_5)_2S\}_4]X_2$, represented by (1) nitritoplatinite, and (2) picrate.

(xxxvi) *Quaterpropylsulphines*, $[Pt\{(C_3H_7)_2S\}_4]X_2$, represented by the chloroplatinite.

(xxxvii) *Quaterbutylsulphines*, $[Pt\{(C_4H_9)_2S\}_4]X_2$, represented by the chloroplatinite with normal and iso-butyl.

(xxxviii) *Bisethylenesulphines*, $[Pt\{S(C_2H_4)_2S\}_2]X_2$, represented by the (1) chloride ; (2) bromide ; (3) iodide ; and (4) sulphate.

(xxxix) *Bisdimethyldithioethyleneglycols*, $[Pt(CH_3.S.C_2H_4.S.CH_3)_2]X_2$, represented by (1) chloroplatinite ; (2) nitritoplatinite ; and (3) nitroprusside.

(xl) *Bisdiethyldithioethyleneglycols*, $[Pt(C_2H_5.S.C_2H_4.S.C_2H_5)_2]X_2$, represented by (1) chloride, chloroplatinite, and chloroplatinate ; (2) bromoplatinite ; (3) nitritoplatinate ; (4) picrate ; (5) picrolonate ; and (6) nitroprusside.

(xli) *Bisdipropyldithioethyleneglycols*, $[Pt(C_3H_7.S.C_2H_4.S.C_3H_7)_2]X_2$, represented by (1) chloroplatinite ; and (2) nitritoplatinite.

(xlii) *Bisdibutyldithioethyleneglycols*, $[Pt(C_4H_9.S.C_2H_4.S.C_4H_9)_2]X_2$, represented by (1) chloroplatinite ; and (2) nitritoplatinite.

(xliii) *Bisdiethyldithiotrimethyleneglycols*, $[Pt(C_2H_5.S.C_3H_6.S.C_2H_5)_2]X_2$, represented by (1) chloroplatinite ; (2) nitritoplatinite ; and (3) nitroprusside.

(xliv) *Bisdipropyldithiotrimethyleneglycols*, $[Pt(C_3H_7.S.C_3H_6.S.C_3H_7)_2]X_2$, represented by the chloroplatinite.

(xlv) *Bisdiethyldithioxydiethylglycols*, $[Pt(C_2H_5.S.CH_2(OH).CH_2.S.C_2H_5)_2]X_2$, represented by (1) chloroplatinite ; and (2) nitritoplatinite.

(xlvi) *Dithioglycolesters.*

(xlvii) *Quaterethylselenines*, $[Pt\{(C_2H_5)_2Se\}_4]X_2$, represented by (1) chloride and chloroplatinite ; (2) sulphate ; and (3) nitrate.

(xlviii) *Bisdiethyldiselenotrimethyleneglycols*, $[Pt(C_2H_5.Se.C_3H_6.Se.C_2H_5)_2]X_2$, represented by (1) picrate ; and (2) nitroprusside.

(xlix) *Quatertrimethylphosphines*, $[Pt\{P(CH_3)_3\}_4]X_2$, represented by the chloride.

(l) *Quatertriethylphosphines*, $[Pt\{P(C_2H_5)_3\}_4]X_2$, represented by the chloride, chlorocuprate, and chloroplatinate.

(li) *Quatertriethylarsines*, $[Pt\{As(C_2H_5)_3\}_4]X_2$, represented by the chloride.

(lii) *Dimethylaminetriammines*, $[Pt(NH_3)_3\{(CH_3)_2NH\}]X_2$, represented by the chloride and chloroplatinite.

(liii) *Pyridinetriammines*, $[Pt(NH_3)_3(C_5H_5N)]X_2$, represented by the chloride and chloroplatinite.

(liv) *Methylsulphinotriammines*, $[Pt(NH_3)_3\{(CH_3)_2S\}]X_2$, represented by the chloride.

(lv) *Ethylsulphinotriammines*, $[Pt(NH_3)_3\{C_2H_5)_2S\}]X_2$, represented by two isomeric chlorides, and chloroplatinite.

(lvi) *Triamminotriethylphosphites*, $[Pt(NH_3)_3\{P(OC_2H_5)_3\}]X_2$, represented by a complex chloride and chloroplatinate.

(lvii) *Bismethylaminediammines*, $[Pt(NH_3)_2(CH_3NH_2)_2]X_2$, represented by the chloride in its cis- and trans-forms.

(lviii) *Bisethylaminediammines*, $[Pt(NH_3)_2(C_2H_5NH_2)_2]X_2$, represented by the cis- and trans-forms of the (1) chloride and the chloroplatinite ; (2) iodide ; (3) sulphate ; and (4) nitrate.

(lix) *Bispropylaminediammines*, $[Pt(NH_3)_2(C_3H_7NH_2)_2]X_2$, represented by the cis- and trans-forms of the chloride.

(lx) *Bisbutylaminediammines*, $[Pt(NH_3)_2(C_4H_9NH_2)_2]X_2$, represented by the chloride.

(lxi) *Bisdimethylaminediammines*, $[Pt(NH_3)_2\{(CH_3)_2NH\}_2]X_2$, represented by the cis- and trans-forms of the (1) chloride and chloroplatinite ; and (2) bromide.

(lxii) *Bisanilinediammines*, $[Pt(NH_3)_2(C_6H_5NH_2)_2]X_2$, represented by the cis- and trans-forms of the (1) chloride and chloroplatinite ; (2) sulphate ; (3) nitrate ; and (4) oxalate.

(lxiii) *Bis-β-methyltrimethylenediamines*, $[Pt\{CH(CH_3)(CH_2.NH_2)_2\}_2]X_2$, represented by (1) bromide ; (2) iodide ; (3) nitrate ; (4) tartrate ; and (5) camphorsulphonates.

(lxiv) *Ethylenediaminediammines*, $[Pt(NH_3)_2\{C_2H_4(NH_2)_2\}]X_2$, represented by the chloride, chloroplatinite, and chloroplatinate.

(lxv) *Propylenediaminediammines*, $[Pt(NH_3)_2\{C_3H_6(NH_2)_2\}]X_2$, represented by the inactive and lævo-forms of the chloride, and chloroplatinite.

(lxvi) *Bispyridinediammines*, $[Pt(NH_3)_2(C_5H_5N)_2]X_2$, represented by the cis- and trans-forms of the chloride and chloroplatinite.

(lxvii) *Bispropionitrilediammines*, $[Pt(NH_3)_2(C_2H_5CN)_2]X_2$, represented by the cyanide.

(lxviii) *Bisaminoacetaldiammines*, $[Pt(NH_3)_2\{NH_2.CH_2.CH(OC_2H_5)_2\}_2]X_2$, represented by the chloride and chloroplatinite.

(lxix) *Bisthiocarbamidiammines*, $[Pt(NH_3)_2\{CS(NH_2)_2\}_2]X_2$, represented by the chloride.

(lxx) *Bisphosphamidodiammines*, $[Pt(NH_3)_2\{P(NH_2)_3\}_2]X_2$, represented by the chloride.

(lxxi) *Biscarbonyldiammines*, $[Pt(NH_3)_2(CO)_2]X_2$, represented by thechloride.

(lxxii) *Bismethylsulphinodiammines*, $[Pt(NH_3)_2\{(CH_3)_2S\}_2X_2$, represented by the chloride.

(lxxiii) *Ethylenesulphinodiammines*, $[Pt(NH_3)_2\{(C_2H_4)_2S_2\}]$, represented by the sulphate.

(lxxiv) *Diamminodiethylthioglycollate*, $[Pt(NH_3)_2\{H.CO_2.CH_2.S(C_2H_5)_2\}]X_2$, represented by the (1) sulphate ; and (2) nitrate.

(lxxv) *Quaterthiocarbamides*, $[Pt\{CS(NH_2)_2\}_4]Cl_2$—see xxvi.

(lxxvi) *Bisthiocarbamidodiammines*, $[Pt\{CS(NH_2)_2\}_2(NH_3)_2]Cl_2$.

(lxxvii) *Bisethylphosphinodiammines*, $[Pt(NH_3)_2\{P(C_2H_5)_3\}_2]X_2$, represented by the chloride and its isomers, and the chloroplatinite.

(lxxviii) *Diamminobismethylphosphite*, $[Pt(NH_3)_2\{P(OCH_3)_3\}_2]X_2$, represented by the chloride.

(lxxix) *Bispyridinedihydroxylamines*, $[Pt(NH_2OH)_2(C_5H_5N)_2]X_2$, represented by the chloroplatinite—see vii.

(lxxx) *Bismethylaminebisethylamines*, $[Pt(CH_3NH_2)_2(C_2H_5NH_2)_2]X_2$, represented by the cis- and trans-chloride.

(lxxxi) *Bismethylaminebispropylamines*, $[Pt(CH_3NH_2)_2(C_3H_7NH_2)_2]X_2$, represented by the cis- and trans-chloride.

(lxxxii) *Bisethylaminebispropylamines*, $[Pt(C_2H_5NH_2)_2(C_3H_7NH_2)_2]X_2$, represented by the cis- and trans-chloride and chloroplatinite.

(lxxxiii) *Ethylenediaminepropylenediamines*, $[Pt\{C_2H_4(NH_2)\}\{C_3H_6(NH_2)_2\}]X_2$, represented by the chloride.

(lxxxiv) *Propylenediaminetrimethylenediamines*, $[Pt\{C_3H_6(NH_2)_2\}\{(CH_2)_3(NH_2)_2\}]X_2$, represented by the chloride.

(lxxxv) *Bisethylaminobispyridines*, $[Pt(C_2H_5NH_2)_2(C_5H_5N)_2]X_2$, represented by the cis- and trans-chloroplatinite.

(lxxxvi) *Bisdimethylaminebispyridines*, $[Pt\{(CH_3)_2NH\}_2(C_5H_5N)_2]X_2$, represented by the chloride and chloroplatinite.

(lxxxvii) *Bispyridinebisthiocarbamides*, $[Pt(C_5H_5N)_2\{CS(NH_2)_2\}_2]X_2$, represented by (1) hydroxide ; (2) chloride.

(lxxxviii) *Bisacetonitrilotetrammines*, $[Pt(NH_3)_4(CH_3.CN)_2]X_2$, represented by (1) the isomeric chlorides and the chloroplatinites ; and (2) the picrates.

(lxxxix) *Bisanilinebismethylphosphites*, $[Pt(C_6H_5NH_2)_2\{P(OCH_3)_3\}_2]X_2$, represented by the chloride.

(xc) *Bisanilinebisethylphosphites*, $[Pt(C_6H_5NH_2)_2\{P(OC_2H_5)_3\}_2]X_2$, represented by the chloride.

(xci) *Bistoluidinebismethylphosphites*, $[Pt(C_7H_9N)_2\{P(OCH_3)_3\}_2]X_2$, represented by the chloride.

(xcii) *Bistoluidinebisethylphosphites*, $[Pt(C_7H_9N)_2\{P(OC_2H_5)_3\}_2]X_2$, represented by the chloride.

3.—**The triammine family,** or compounds of the univalent group $[PtA_3X]'$.

(i) *Hydroxytriammines*, $[Pt(NH_3)_3(OH)]X$, represented by the hydroxide.

(ii) *Chlorotriammines*, $[Pt(NH_3)_3Cl]X$, represented by the chloride, chloroplatinite, and chloroplatinate.

(iii) *Sulphatotriammines*, $Pt(NH_3)_3SO_4$.

(iv) *Nitritodihydroxylammines*, $[Pt(NH_3)(NH_2OH)_2(NO_2)]X$, represented by the chloride and chloroplatinite—see x.

(v) *Nitritohydroxylaminopyridinoammines*, $[Pt(NH_3)py(NH_2OH)(NO_2)]X$, represented by the chloride, and chloroplatinite, and nitrite—see x.

(vi) *Nitritoethylenediaminoammines*, $[Pt(NH_3)en(NO_2)]X$, represented by the hydroxide—see x.

(vii) *Nitritopyridinodiammines*, $[Pt(NH_3)_2py(NO_2)]X$, represented by the chloride and chloroplatinite—see x.

(viii) *Nitritoethylenediaminoammine*, $[Pt(NH_3)en(NO_2)]X$, represented by the chloroplatinite—see x.

(ix) *Nitratotriammines*, $[Pt(NH_3)_3(NO_3)]X$, represented by the nitrate.

(x) *Nitritotriammines*, $[PtA_3(NO_2)]X$, *e.g.* nitritotrihydroxylaminochloroplatinite, $[Pt(NH_2OH)_3(NO_2)]PtCl_4$; nitritodihydroxylaminoamminochloroplatinite, $[Pt(NH_3)(NH_2OH)_2(NO_2)]PtCl_4$; nitritohydroxylaminodiamminochloroplatinite, $[Pt(NH_3)_2(NH_2OH)(NO_2)]PtCl_4$; nitritoethylenediaminoamminochloroplatinite, $[Pt(NH_3)en(NO_2)]PtCl_4$; nitritopyridinediamminochloroplatinite, $[Pt(NH_3)_2py(NO_2)]PtCl_4$, and its isomerides ; nitritobispyridinoamminochloroplatinite, $[Pt(NH_3)py_2(NO_2)]PtCl_4$; nitritopyridinohydroxylaminoamminochloroplatinite, $[Pt(NH_3)(NH_2OH)py(NO_2)]PtCl_4$, and its isomerides ; nitritopyridinomethylaminoamminochloroplatinite, $[Pt(NH_3)(CH_3NH_2)py(NO_2)]PtCl_4$; along with the complexes : $[(NH_3)_2(NO_2)Pt(NH_2.CH_2.CH_2.NH_2)Pt(NH_3)_2(NO)]PtCl_4$; $[(NH_3)(NH_2OH)(NO_2)Pt(NH_2.CH_2.CH_2.NH_2)Pt(NO_2)(NH_2OH)(NH_3)]PtCl$; $[(NH_3)py(NO_2)Pt(NH_2.CH_2.CH_2.NH_2)Pt(NO_2)py(NH_3)]PtCl_4$; $[(NH_3)(NH_2OH)(NO_2)Pt(NH_2 : NH_2)Pt(NO_2)(NH_2OH)(NH_3)]SO_4$; and $[(NH_3)_2(NO_2)Pt(NH_2 : NH_2)Pt(NO_2)(NH_3)_2]SO_4$.

(xi) *Oxalatotriammines*, $Pt(NH_3)_3(C_2O_4)$.

(xii) *Chloroglycinodiammines*, $Pt(NH_3)_2(C_2H_5O_2N)Cl$, represented by (1) chloride, and chloroplatinite ; (2) hydrochloride ; (3) hydrobromide ; and (4) hydroiodide.

(xiii) *Chlorotricarbonyls*, $[Pt(CO)_3Cl]X$, represented by the chloroplatinate.

(xiv) *Nitritoethylenediaminoammine*, $[Pt(NH_3)en(NO_2)]X$, represented by the chloride—see x.

(xv) *Chlorotrimethylsulphines*, $[Pt\{(CH_3)_2S\}_3Cl]X$, represented by the chloroplatinate.
(xvi) *Chlorotrisethylsulphines*, $[Pt\{(C_2H_5)_2S\}_3Cl]X$, represented by the chloride.
(xvii) *Sulphatotrisethylsulphines*, $[Pt\{(C_2H_5)_2S\}_3SO_4$.
(xviii) *Nitritotrisethylsulphines*, $[Pt\{(C_2H_5)_2S\}_3NO_3]X$, represented by the nitrate.
(xix) *Sulphatobutylsulphines*, $[Pt\{(C_4H_9)_2S\}_3SO_4]$.
(xx) *Chloroethylenesulphines*, $[Pt_2\{(C_2H_4)_2S_2\}_3Cl_2]X_2$, represented by the chloride.
(xxi) *Chlorotrisethylsulphines*, $[Pt\{(C_2H_5)_2S\}_3Cl]X$, represented by the chloride.
(xxii) *Sulphatotrisethylsulphines*, $[Pt\{(C_2H_5)_2Se\}_3]SO_4$.
(xxiii) *Chloroanilinediammines*, $[Pt(NH_3)_2(C_6H_5NH_2)Cl]X$, represented by the chloride and chloroplatinite.
(xxiv) *Chlorophosphaminediammine*, $[Pt(NH_3)_2(C_6H_5NH_2)Cl]X$, represented by the double salt with ammonium chloride.
(xxv) *Chlorocarbonyldiammines*, $[Pt(NH_3)_2(CO)Cl]X$, represented by the chloride.
(xxvi) *Chloroethylsulphinediammines*, $[Pt(NH_3)_2\{(C_2H_5)_2S\}Cl]X$, represented by the (1) chloride and chloroplatinite ; and (2) ethylmercaptide.
(xxvii) *Iodoethylenesulphinediammines*, $[Pt(NH_3)_2\{(C_2H_4)_2S_2\}I]X$, represented by the iodide, and the iodochloroplatinite.
(xxviii) *Chlorodiamminoethylphosphites*, $[Pt(NH_3)_2\{P(OC_2H_5)_3\}Cl]X$, represented by the chloride and the chloroplatinite.
(xxix) *Chlorobisanilineethylphosphite*, $[Pt(C_6H_5NH_2)_2\{P(OC_2H_5)_3\}Cl]X$, represented by the chloride.
(xxx) *Chlorobistoluidineethylphosphite*, $[Pt(C_7H_9N)_2\{P(OC_2H_5)_3\}Cl]X$, represented by the chloride.

4.—**The diammine family** represented by the null-valent group $[PtA_2X_2]$.

(i) *Diammines*, $[Pt(NH_3)_2X_2]$, illustrated by various cis- and trans-forms of (1) oxide ; (2) hydroxide ; (3) chloride and double salt with ammonium chloride ; (4) hydroxychloride ; (5) bromide ; (6) iodide ; (7) chlorosulphite ; (8) sulphite-double salts with the sulphites of ammonium, sodium, copper, silver, barium, zinc, lead, uranyl, manganese, cobalt, and nickel, chlorosulphites, and ammonium chlorosulphites ; (9) chlorohydrosulphite ; (10) sulphate ; (11) nitrite, and nitritoplatinite ; (12) nitrate ; (13) chlorocarbonate ; (14) thiocarbonate ; (15) chlorothiocarbonate ; (16) oxalate ; (17) cyanide and cyanoplatinite ; (18) thiocyanate and the double salt with silver thiocyanate ; (19) mercaptides and chloromercaptides, iodomercaptides, and sulphatomercaptides ; (20) xanthogenate ; and (21) ethylthioglycolate ; and nitratoethylthioglycolate.
(ii) *Dihydrazines*, $[Pt(N_2H_4)_2X_2]$, represented by the chloride.
(iii) *Dihydroxylamines*, $[Pt(NH_2OH)_2X_2]$, represented by various cis- and trans-forms of the (1) oxide ; (2) hydroxide ; and (3) chloride.
(iv) *Hydroxylaminoammines*, $[Pt(NH_3)(NH_2OH)X_2]$, represented by the chloride.
(v) *Bismethylamines*, $[Pt(CH_3NH_2)_2X_2]$, represented by the (1) chloride ; and (2) bromide.
(vi) *Bisethylamines*, $[Pt(C_2H_5NH_2)_2X_2]$, represented by the cis- and trans-forms of (1) chloride ; and (2) bromide.
(vii) *Bisdiethylamines*, $[Pt\{(C_2H_5)_2NH\}_2Cl_2]$, and also a complex with acetone, $PtCl_2(C_2H_5)_2NH.(CH_3)_2CO$.
(viii) *Bispropylamines*, $[Pt(C_3H_7NH_2)_2X_2]$, represented by (1) chloride ; and (2) iodide.

(ix) *Bisdimethylamines*, $[Pt\{(CH_3)_2NH\}_2X_2]$, represented by (1) chloride; (2) bromide; and (3) nitrate.

(x) *αβγ-triaminopropanes*, $[Pt\{NH_2.CH_2.CH(NH_2).CH_2NH_2\}_2Cl_2]$, represented by (1) chloride; (2) bromide; (3) iodide; and (4) picrate; as well as compounds with one of the base replaced by hydrogen chloride, camphor sulphonates, oxalic acid, and thiocyanic acid.

(xi) *Bisanilines*, $[Pt(C_6H_5NH_2)_2X_2]$, represented by (1) chloride; (2) sulphite and double salts with silver and barium sulphites; and (3) hydrosulphites.

(xii) *Bistoluidines*, $[Pt(C_7H_7NH_2)_2X_2]$, represented by the chloride.

(xiii) *Bisxylidines*, $[Pt(C_8H_9NH_2)_2X_2]$, represented by the chloride.

(xiv) *Ethylenediamines*, $[Pt\{C_2H_4(NH_2)_2\}X_2]$, represented by the cis- and trans-chloride.

(xv) *Propylenediamines*, $[Pt\{C_3H_6(NH_2)_2\}X_2]$, represented by the chloride.

(xvi) *Toluylenediamines*, $[Pt\{C_7H_6(NH_2)_2\}X_2]$, represented by the chloride.

(xvii) *m-tolylenediammines*, $[Pt(C_7H_{10}N_2)X_2]$, represented by the chloride.

(xviii) *Bispyridines*, $[Pt\{(C_5H_5N)_2\}X_2]$, represented by cis- and trans-forms of (1) hydroxide; (2) fluoride; (3) chloride; (4) bromide; (5) iodide; (6) sulphite and sulphitoplatinites; (7) hydrosulphite; (8) sulphate; (9) hydroxysulphate; (10) nitrite; (11) nitrate; (12) carbonate; (13) thiocyanate; and (14) phenylmercaptide.

(xix) *Bis-2-amino-l-acetylpyridines*, $[Pt(C_7H_8ON_2)_2X_2]$, represented by the chloride.

(xx) *Bis-3-aminopyridines*, $[Pt(C_5H_6N_2)_2X_2]$, represented by the chloride.

(xxi) *Bispiperidines*, $[Pt(C_5H_{11}N)_2X_2]$, represented by the chloride.

(xxii) *Bisquinolines*, $[Pt(C_9H_7N)_2X_2]$, represented by the chloride.

(xxiii) *Bisacetonitriles*, $[Pt(CH_3.CN)_2X_2]$, represented by the chloride.

(xxiv) *Bismethylcarbylamines*, $[Pt(CH_3.NC)_2X_2]$, represented by the (1) chloride; and (2) cyanide.

(xxv) *Bispropionitriles*, $[Pt(C_2H_5.CN)_2X_2]$, represented by the cyanide.

(xxvi) *Bisethylcarbylamines*, $[Pt(C_2H_5.NC)_2X_2]$, represented by the cyanide.

(xxvii) *Bisbutylcarbylamines*, $[Pt(C_4H_9.NC)_2X_2]$, represented by (1) chloride; and (2) cyanide.

(xxviii) *Bisbenzonitriles*, $[Pt(C_6H_5.CN)_2X_2]$, represented by the (1) chloride and complexes with chloroform, and benzene; (2) bromide; and (3) iodide.

(xxix) *Bisphenylcarbylamines*, $[Pt(C_6H_5NC)_2X_2]$, represented by (1) chloride; (2) bromide; (3) iodide; (4) polyiodide; and (5) nitrite.

(xxx) *Bisamidoacetates*, $[Pt(NH_2.CH_2.COOH)_2X_2]$, represented by (1) chloride; (2) bromide; and (3) iodide.

(xxxi) *Bisamidomethylacetates*, $[Pt(NH_2.CH_2.COOCH_3)_2X_2]$, represented by the chloride.

(xxxii) *Bisamidoethylacetates*, $[Pt(NH_2.CH_2.COOC_2H_5)_2X_2]$, represented by (1) chloride; and (2) bromide.

(xxxiii) *Bisamidoacetals*, $[Pt\{NH_2.CH_2.CH(OC_2H_5)_2\}_2X_2]$, represented by the chloride.

(xxxiv) *Bisthioacetamides*, $[Pt(CH_3.CS.NH_2)_2X_2]$, represented by the chloride.

(xxxv) *Bisthiocarbamides*, $[Pt\{CS(NH_2)_2\}_2X_2]$, represented by the chloride.

(xxxvi) *Dicarbonyls*, $[Pt(CO)_2X_2]$, represented by the chloride.

(xxxvii) *Diphosgenes*, $[Pt(COCl_2)_2X_2]$, represented by the chloride.

(xxxviii) *Bisdimethylsulphines*, $[Pt\{(CH_3)_2S\}_2X_2]$, represented by cis- and trans-forms of (1) hydroxide; (2) chloride, chloroplatinite, and a complex with chloroform; (3) bromide; (4) iodide; (5) sulphate; (6) nitrite; (7) nitrate; (8) phosphate; (9) borate; (10) carbonate; (11) cyanide; (12) thiocyanate; (13) nitroprusside; and (14) chromate.

(xxxix) *Bisdiethylsulphines*, $[Pt\{(C_2H_5)_2S\}_2X_2]$, represented by cis- and trans-forms of (1) hydroxide; (2) chloride and chloroplatinite; (3) bromide; (4) iodide; (5) sulphate; (6) nitrite; (7) nitrate; (8) phosphate; (9) oxalate; (10) chromate; and (11) dichromate.

(xl) *Methylethylsulphines*, $[Pt\{(CH_3)(C_2H_5)S\}_2X_2]$, represented by the iodide.

(xli) *Diethylaminoethylsulphines*, $[Pt(C_2H_5)_2S.(C_2H_5)_2NH]X_2$, represented by the chloride.

(xlii) *Bisdipropylsulphines*, $[Pt\{(C_3H_7)_2S\}_2X_2]$, with normal and iso-propyl cis- and trans-forms of (1) hydroxide; (2) chloride, double salts with mercuric, stannous, and platinous chloride, and hydroxy-chloride; (3) bromide; (4) iodide and iodoplatinite; (5) chloro-iodide; (6) sulphate; (7) thiosulphate; (8) nitrite; (9) nitrate and hydroxynitrate; (10) oxalate; (11) cyanide; (12) thiocyanate; and (13) chromate.

(xliii) *Bisbutylsulphines*, $[Pt\{(C_4H_9)_2S\}_2X_2]$, represented by the normal, iso-, and secondary butyl cis- and trans-forms of (1) hydroxide; (2) chloride and complexes with chloroform and with carbon disulphide; (3) bromide; (4) iodide; (5) sulphide; (6) sulphate; (7) nitrite; (8) nitrate; (9) chloronitrate; and (10) chromate.

(xliv) *Bis-iso-amylsulphines*, $[Pt\{(C_5H_{11})_2S\}_2X_2]$, represented by the (1) chloride; and (2) iodide.

(xlv) *Bisbenzylsulphines*, $[Pt\{C_6H_5.CH_2)_2S\}_2X_2]$, represented by (1) chloride, and a complex with chloroform; (2) bromide, and complexes with ethyl alcohol, and with chloroform; (3) iodide; (4) sulphate; (5) nitrite and complex with chloroform; and (6) hydroxynitrate.

(xlvi) *Ethylenedisulphines*, $[Pt\{(C_2H_4)_2S_2\}X_2]$, represented by (1) hydroxide; (2) chloride; (3) bromide; (4) iodide; (5) sulphate; (6) hydroxy-sulphate; (7) nitrite; (8) nitrate; (9) oxalate; (10) cyanide; (11) thiocyanate; (12) chromate; and (13) permanganate.

(xlvii) *Dimethyldithioethyleneglycols*, $[Pt(CH_3.S.C_2H_4.S.CH_3)X_2]$, represented by (1) chloride; and (2) nitrate.

(xlviii) *Diethyldithioethyleneglycols*, $[Pt(C_2H_5.S.C_2H_4.S.C_2H_5)X_2]$, represented by (1) chloride; (2) bromide; (3) nitrite; and (4) nitroprusside.

(xlix) *Dipropylthioethyleneglycols*, $[Pt(C_3H_7.S.C_2H_4S.C_3H_7)X_2]$, represented by (1) chloride; and (2) nitrite.

(l) *Dibutylthioethyleneglycols*, $[Pt(C_4H_9.S.C_2H_4.S.C_4H_9)X_2]$, represented by (1) chloride; and (2) nitrite.

(li) *Diethylpropylenesulphines*, $Pt(C_2H_5.S.C_3H_6.S.C_2H_5)X_2]$, represented by (1) chloride; and (2) nitrite.

(lii) *Dipropylpropylenesulphines*, $[Pt(C_3H_7.S.C_3H_6.S.C_3H_7)X_2]$, represented by the chloride.

(liii) *Diethyldithioxydiethylsulphines*, $[Pt(C_2H_5.S.CH_2.CH(OH).CH_2.S.C_2H_5)$-$X_2]$, represented by (1) chloride; and (2) nitrate.

(liv) *Bisethylthioglycollic acid*, $[Pt(CH_2.S.C_2H_5.COOH)_2X_2]$, represented by the cis- and trans-forms of the chloride.

(lv) *Bisethylmethylthioglycollate*, $[Pt(CH_2.S.C_2H_5.COOCH_3)_2X_2]$, represented by (1) the cis- and trans-forms of the chloride, and (2) oxalate.

(lvi) *Bisthioglycollic acid*, $[Pt\{S(CH_2.COOH)_2\}_2X_2]$, represented by (1) chloride; (2) bromide; (3) iodide, and a complex with the potassium salt; (4) cyanide; and (5) thiocyanate.

(lvii) *Bissodiumthioglycollate*, $[Pt\{S(CH_2.COONa)_2\}_2X_2]$, represented by the nitrite.

(lviii) *Bispotassiumthioglycollate*, $[Pt\{S(CH_2.COOK)_2\}_2X_2]$, represented by (1) chloride; (2) bromide; and (3) iodide.

(lix) *Bisbariumthioglycollate*, $[Pt\{S(CH_2.COO)_2Ba\}_2X_2]$, represented by the chloride.

(lx) *Bismethylthioglycollate*, $[Pt\{S(CH_2.COOCH_3)_2\}_2X_2]$, represented by the chloride.

(lxi) *Bisethylthioglycollate*, $[Pt\{S(CH_2.COOC_2H_5)_2\}_2X_2]$, represented by the chloride.

(lxii) *Ethylenethioglycollic acid*, $[Pt\{C_2H_4(S.CH_2.COOH)_2\}X_2]$, represented by the chloride.

(lxiii) *Ethylenepotassiumthioglycollate*, $[Pt\{C_2H_4(S.CH_2.COOK)_2\}X_2]$, represented by the chloride.

(lxiv) *Bisdiethylselenines*, $[Pt\{(C_2H_5)_2Se\}_2X_2]$, represented by cis- and trans-forms of (1) chloride and double salts with mercuric and platinous chlorides; (2) bromide and the bromoplatinite; (3) chlorobromide; (4) iodide; (5) chloroiodide; (6) bromoiodide; (7) sulphate; (8) nitrite; (9) nitrate; (10) thiocyanate; and (11) chromate.

(lxv) *Bisphosphorous acid*, $[Pt\{P(OH)_3\}_2X_2]$, represented by the chloride.

(lxvi) *Bisphosphorustrichloride*, $[Pt(PCl_3)_2X_2]$, represented by the chloride.

(lxvii) *Bisphosphorustribromide*, $[Pt(PBr_3)_2X_2]$, represented by the bromide.

(lxviii) *Bistrimethylphosphines*, $[Pt\{P(CH_3)_3\}_2X_2]$, represented by the cis- and trans-chlorides.

(lxix) *Bistriethylphosphines*, $[Pt\{P(C_2H_5)_3\}_2X_2]$, represented by the cis- and trans-chlorides, and a complex with phenylmercaptide.

(lxx) *Bistrimethylphosphite*, $[Pt\{P(OCH_3)_3\}_2X_2]$, represented by the (1) chloride; and (2) bromide.

(lxxi) *Bistriethylphosphite*, $[Pt\{P(OC_2H_5)_3\}_2X_2]$, represented by the chloride.

(lxxii) *Bistriphenylphosphite*, $[Pt\{P(OC_6H_5)_3\}_2X_2]$, represented by the chloride.

(lxxiii) *Bissilverphosphite*, $[Pt\{P(OAg)_3\}_2X_2]$, represented by the chloride.

(lxxiv) *Bistriethylarsines*, $[Pt\{As(C_2H_5)_3\}_2X_2]$, represented by the cis- and trans-chlorides.

(lxxv) *Bistriethylstibines*, $[Pt\{Sb(C_2H_5)_3\}_2X_2]$, represented by the chloride.

(lxxvi) *Bisacetamides*, $[Pt(NH_2.CO.CH_3)_2X_2]$.

(lxxvii) *Bisamidoacetate*, $[Pt(NH_2.CH_2.CO_2)_2]$.

(lxxviii) *Bis-a-amidoproprionate*, $[Pt(NH_2.CH_3.CH.CO_2)_2]$.

(lxxix) *Bismethylethylglyoximine*, $[Pt(NO.C.C_2H_5CH_3.C.NOH)_2]$.

(lxxx) *Bismethylpropylglyoximine*, $[Pt(NO:C.C_3H_7CH_3.C.NOH)_2]$.

(lxxxi) *Bismethyl-iso-butylglyoximine*, $[Pt(NO:C.C_4H_9CH_3.C.NOH)_2]$.

(lxxxii) *Bisdiphenylglyoximine*, $Pt(NO:C.C_6H_5C_6H_5.C.NOH)_2]$.

(lxxxiii) *Bisethylthioglycolate*, $[Pt(CO_2.CH_2.S.C_2H_5)_2]$, represented by the cis- and trans-forms.

(lxxxiv) *Chlorobisethylthioglycollate*, $[Pt(HCO_2.CH_2.S.C_2H_5)(CO_2.CH_2S.C_2H_5)Cl]$.

(lxxxv) *Nitratoethylthioglycollatoammines*, $[Pt(NH_3)(CO_2.CH_2.S.C_2H_5)(NO_3)]$.

(lxxxvi) *Bisdiphenylthioglycolate*, $[Pt(CO_2.CH_2.S.C_6H_5)_2]$.

(lxxxvii) *Ethylenethioglycollate*, $[Pt\{C_2H_4(S.CH_2.CO_2)_2\}]$.

(lxxxviii) *Bisethylenethioglycollate*, $[Pt\{C_2H_4(S.CH_2.CO_2)_2\}_2X_2]$, represented by the acid and the sodium salt.

(lxxxix) *Bisthiodiglycollate*, $[Pt\{S(CH_2COOH)_2\}_2]$, represented by (1) acid; and the salts; (2) methyl; (3) potassium; (4) sodium; (5) silver; (6) calcium; and (7) barium.

(xc) *Bisthioglycollate*, $[Pt\{S(CH_2COOR)_2\}(RO.CO.CH_2S.CH_2COOR)X]$, represented by (1) hydrochloride and the potassium salt; (2) hydrobromide and the potassium and barium salts; (3) hydroiodide, and

the potassium salt ; (4) hydrosulphite and the potassium and sodium salts ; (5) hydronitrite and the sodium salt ; (6) hydrocyanide and the potassium salt ; (7) hydrothiocyanate.

(xci) *Bisxanthogenates*, $[Pt(S.CS.OC_2H_5)_2X_2]$.

(xcii) *Dithiocyanates*, $[PtA_2(SCN)_2]$, *e.g. dithiocyanatodiammine*, $[Pt(NH_3)_2(SCN)_2]$, with cis- and trans-forms, and a complex with silver nitrate ; *dithiocyanatobispyridine*, $[Pt\ py_2(SCN)_2]$; and *dithiocyanatoethylenediamine*, $[Pt\ en(SCN)_2]$.

(xciii) *Hydroxylamineammines*, $[Pt(NH_3)(NH_2OH)X_2]$, represented by the chloride.

(xciv) *Dinitrito-complexes*, $[PtA_2(NO_2)_2]$, *e.g.* dinitritodihydroxylamine, $[Pt(NH_2OH)_2(NO_2)_2]$, and its isomerides ; dinitritodiammine, $[Pt(NH_3)_2(NO_2)_2]$; dinitritohydroxylaminoammines, $[Pt(NH_3)(NH_2OH)(NO_2)_2]$; dinitritopyridinoammine, $[Pt(NH_3)\ py(NO_2)_2]$; dinitritohydroxylaminopyridine, $[Pt(NH_2OH)\ py(NO_2)_2]$; dinitritoethylenediamine, $[Pt\ en(NO_2)_2]$.

(xcv) *Chloronitrito-complexes*, $[PtA_2(NO_2)Cl]$, *e.g.* chloronitritodihydroxylamine, $[Pt(NH_2OH)_2(NO_2)Cl]$; chloronitritohydroxylaminoammine, $[Pt(NH_3)(NH_2OH)(NO_2)Cl]$; chloronitritohydroxylaminopyridine, $[Pt\ py(NH_2OH)(NO_2)Cl]$; chloronitritopyridinoammine, $[Pt(NH_3)\ py(NO_2)Cl]$; chloronitritoethylenediamine, $[Pt\ en(NO_2)Cl]$; and chloronitritodiammine, $[Pt(NH_3)_2(NO_2)Cl]$.

(xcvi) *Ethylamineammines*, $[Pt(NH_3)(C_2H_5NH_2)X_2]$, represented by the (1) chloride ; (2) bromide ; and (3) iodide.

(xcvii) *Dimethylamineammines*, $[Pt(NH_3)\{(CH_3)_2NH\}X_2]$, represented by the bromide.

(xcviii) *Dimethylanilinoammines*, $Pt(NH_3)\{(CH_3)_2[C_6H_5N\}Cl_2]$.

(xcix) *Anilineammines*, $[Pt(NH_3)(C_2H_5NH_2)X_2]$, represented by the iodide.

(c) *Pyridineammines*, $[Pt(NH_3)(C_5H_5N)X_2]$, represented by the cis- and trans-forms of the chloride ; and (2) the hydrosulphitochloride.

(ci) *Bis-m-tolylenediamines*, $[Pt(C_7H_{10}N_2)_2]X_2$, represented by (1) chloride ; (2) sulphate ; and (3) dithionate.

(cii) *Ethyleneammines*, $[Pt(NH_3)(C_2H_4)X_2]$, represented by the chloride.

(ciii) *Ethylsulphineammines*, $[Pt(NH_3)\{(C_2H_5)_2S\}X_2$, represented by the cis- and trans-forms of the iodide.

(civ) *Ethylaminehydroxylamines*, $[Pt(NH_2OH)(C_2H_5NH_2)X_2]$, represented by the oxide.

(cv) *Pyridinehydroxylamines*, $[Pt(NH_2OH)(C_5H_5N)X_2]$, represented by the chloride.

(cvi) *Ethylenediethylamines*, $[Pt(C_2H_4)\{(C_2H_5)_2NH\}X_2]$, represented by the chloride.

(cvii) *Ethyleneanilines*, $[Pt(C_6H_5NH_2)(C_2H_4)X_2]$, represented by the chloride.

(cviii) *Anilinetrimethylphosphite*, $[Pt(C_6H_5NH_2)\{P(OCH_3)_2\}X_2]$, represented by the chloride.

(cix) *Anilinetriethylphosphite*, $[Pt(C_6H_5NH_2)\{P(OC_2H_5)_3\}X_2]$, represented by the cis- and trans-forms of (1) chloride ; and (2) bromide.

(cx) *Toluidinetrimethylphosphite*, $[Pt(C_7H_7NH_2\{P(OCH_3)_3\}X_2]$, represented by the chloride.

(cxi) *Toluidinetriethylphosphate*, $[Pt(C_7H_7NH_2)\{P(OC_2H_5)_3\}X_2]$, represented by (1) hydroxide ; (2) cis- and trans-forms of the chloride ; and (3) hydroxychloride.

(cxii) *Pyridines*, $PtCl_2.3C_5H_{11}N$.

(cxiii) *Ethylenediaminebisethylenes*, $[Pt_2\ en(C_2H_4)_2X_4]$, represented by the chloride.

(cxiv) *Carbonylphenylhydrazines*, $[Pt(C_6H_5.N_2H_3)(CO)X_2]$, represented by the chloride.

(cxv) *Pyridinepiperidines*, $[Pt(C_5H_5N)(C_5H_{11}N)X_2]$, represented by the chloride.

(cxvi) *Carbonylpyridines*, $[Pt(C_5H_5N)(CO)X_2]$, represented by (1) chloride; and (2) bromide.

(cxvii) *Pyridineethylsulphines*, $[Pt(C_5H_5N)\{(C_2H_5)_2S\}X_2]$, represented by the cis- and trans-forms of the chloride.

(cxviii) *Pyridineethylselenines*, $[Pt(C_5H_5N)\{(C_2H_5)_2Se\}X_2]$, represented by (1) chloride; (2) bromide; (3) iodide; (4) sulphate; and (5) nitrate.

(cxix) *Pyridinetriethylphosphite*, $[Pt(C_5H_5N)\{P(OC_2H_5)_3\}X_2]$, represented by the cis- and trans-chloride.

(cxx) *Phosphorotrianilidephosphoroxyanilide*, $[Pt\{P(C_6H_6N)_3\}\{PO(C_6H_6N)\}X_2]$, represented by the hydroxychloride.

(cxxi) *Phosphorotritoluididephosphoroxytoluidide*, $[Pt\{P(C_7H_8N)_3\}\{PO(C_7H_8N)\}X_2]$, represented by the hydroxychloride.

(cxxii) *Carbonylethylenes*, $[Pt(C_2H_4)(CO)X_2]$, represented by the chloride.

(cxxiii) *Ethylenetriethylphosphite*, $[Pt_2(C_2H_4)\{P(OC_2H_5)_3\}_2X_4]$, represented by the chloride.

(cxxiv) *Carbonyltriethylphosphite*, $[Pt(CO)\{P(OC_2H_5)_3\}X_2]$, represented by the chloride.

(cxxv) *Methylethylsulphines*, $[Pt\{(CH_3)_2S\}\{(C_2H_5)_2S\}X_2]$, represented by the chloride.

(cxxvi) *Ethylpropylsulphines*, $[Pt\{(C_2H_5)_2S\}\{(C_3H_7)_2S\}X_2]$, with normal and iso-propyl (1) chloride; (2) bromide; (3) iodide; (4) sulphate; and (5) nitrite.

(cxxvii) *Ethylbutylsulphines*, $[Pt\{(C_2H_5)_2S\}\{(C_4H_9)_2S\}X_2]$, represented by (1) chloride and complex with chloroform; and (2) iodide.

(cxxviii) *n-Propyl-i-propylsulphines*, $[Pt\{(C_3H_7)_2S\}X_2]$, represented by the iodide.

(cxxix) *Benzylsulphines*, $PtCl_2.2(CH_2.C_6H_5)_2S$.

(cxxx) *Diethylenedisulphines*, $PtCl_2.(C_2H_4)_2S_2$.

(cxxxi) *Ethylsulphineethylselenines*, $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}X_2]$, represented by (1) cis- and trans-forms of the chloride and chloroplatinite; (2) bromide; (3) chlorobromide; (4) iodide; (5) chloriodide; (6) sulphate; (7) nitrite; (8) nitrate; and (9) chloronitrate.

(cxxxii) *Phosphorohydroxytriethylphosphite*, $[Pt\{P(OH)_3\}\{P(OC_2H_5)_3\}X_2]$, represented by the chloride.

(cxxxiii) *Phosphorochloridetriethylphosphite*, $[Pt(PCl_3)\{P(OC_2H_5)_3\}X_2]$, represented by the chloride.

(cxxxiv) *Trimethylphosphitetriethylphosphite*, $[Pt\{P(OCH_3)_3\}\{P(OC_2H_5)_3\}X_2]$, represented by the chloride.

5.—**The monammine family** of the type $[PtAX_2]_2$, a null-valent group.

(i) *Ammines*, $[Pt(NH_3)X_2]_2$, represented by (1) chloride; (2) chloromercaptide and chloromercaptide platinite; (3) iodomercaptide; (4) pyrothiocarbonate; and (5) thiocyanate.

(ii) *Hydroxylamines*, $[Pt(NH_2OH)X_2]_2$, represented by the hydroxide.

(iii) *Ethylamines*, $[Pt(C_2H_5NH_2)X_2]_2$, represented by the chloride.

(iv) *Pyridines*, $[Pt(C_5H_5N)X_2]_2$, represented by the chloride.

(v) *Thiocarbamides*, $[Pt\{CS(NH_2)_2\}X_2]_2$, represented by the chloride.

(vi) *Phosphorotrianilides*, $[Pt\{P(C_6H_6N)_3\}X_2]_2$, represented by the hydroxychloride.

(vii) *Phosphorotritoluidides*, $[Pt\{P(C_7H_8N)_3\}X_2]_2$, represented by the hydroxychloride.

(viii) *Ethylenes*, $[Pt(C_2H_4)X_2]_2$, represented by the chloride.

(ix) *Carbonyls*, $[Pt(CO)X_2]_2$, represented by the (1) oxide; (2) chloride; (3) bromide; (4) iodide; (5) sulphide; (6) hydrosulphide; (7) cyanide; and (8) chlorovinyl.

(x) *Oxymesityls*, $[Pt(C_6H_{10}O)X_2]_2$, represented by the chloride.
(xi) *Ethylsulphines*, $[Pt\{(C_2H_5)_2S\}X_2]_2$, represented by (1) chloride; (2) ethylmercaptan; and (3) chloroethylmercaptan.
(xii) *Phosphorohydroxides*, $[Pt\{P(OH)_3\}X_2]_2$, represented by the (1) chloride; and (2) chlorophosphite.
(xiii) *Phosphorochlorides*, $[Pt(PCl_3)X_2]_2$, represented by the chloride and chloroplatinite.
(xiv) *Phosphorobromides*, $[Pt(PBr_3)X_2]_2$, represented by the bromide.
(xv) *Trimethylphosphites*, $[Pt\{P(OCH_3)_3\}X_2]_2$, represented by the chloride.
(xvi) *Triethylphosphites*, $[Pt\{P(OC_2H_5)_3\}X_2]_2$, represented by (1) hydroxide; (2) chloride and chloroplatinite; (3) bromide; (4) nitrate; and (5) chloronitrate.
(xvii) *Tripropylphosphites*, $[Pt\{P(OC_3H_7)_3\}X_2]_2$, represented by the chloride.
(xviii) *Allylphosphites*, $[Pt\{P(OH)_2(OC_3H_5)\}X_2]_2$, represented by the chloride.
(xix) *Potassiumphosphites*, $[Pt\{P(OK)_3\}X_2]_2$, represented by the oxide.
(xx) *Sodiumphosphites*, $[Pt\{P(ONa)_3\}X_2]_2$, represented by the oxide.
(xxi) *Silverphosphites*, $[Pt\{P(OAg)_3\}X_2]_2$, represented by the chloride, and phosphochloride. There is also $[Pt\{P(OH)(OAg)_2\}Cl_2]_2$.
(xxii) *Leadphosphites*, $[Pt\{P_2(O_2Pb)_3\}X_2]_2$, represented by the chloride.
(xxiii) *Oxycacodyls*, $[Pt\{As_2(CH_3)_4O\}X_2]_2$, represented by (1) chloride; (2) bromide; (3) iodide; (4) sulphate; and (5) nitrate.

6.—**The monammine family** of the type $[PtAX_3]'$, a univalent acidic group.

(i) *Trichloroammines*, $[Pt(NH_3)Cl_3]R$, represented by (1) acid; (2) ammonium; (3) potassium; (4) silver; and (5) platinoustetrammine.
(ii) *Trichlorotrimethylamines*, $[Pt\{(CH_3)_3N\}Cl_3]R$, represented by allyl salt.
(iii) *Trichloroethylamines*, $[Pt\{(C_2H_5)NH_2\}Cl_3]R$, represented by (1) potassium; and (2) platinoustetrammine salts.
(iv) *Trichloroallylamines*, $[Pt\{(C_3H_5)NH_2\}Cl_3]R$, represented by the acid.
(v) *Trichloroethylallylamines*, $[Pt\{(C_2H_5)(C_3H_5)NH\}Cl_3]R$, represented by the acid.
(vi) *Trichlorodiethylallylamines*, $[Pt\{(C_2H_5)_2(C_3H_5)N\}Cl_3]R$, represented by the acid.
(vii) *Trichlorodipropylallylamines*, $[Pt\{(C_3H_7)_2(C_3H_5)N\}Cl_3]R$, represented by the acid.
(viii) *Trinitritotoluidines*, $[Pt(C_7H_9N)(NO_2)_3]R$, represented by the toluidine salt.
(ix) *Hexachloroethylenediamines*, $[Pt_2(NH_2.C_2H_4.NH_2)Cl_6]R_2$, represented by the ethylenediamine salt.
(x) *Trichloropyridines*, $[Pt(C_5H_5N)Cl_3]R$, represented by the (1) ammonium; (2) pyridine; (3) potassium; (4) rubidium; (5) cæsium; and (6) platinoustetrammine salts.
(xi) *Dichloramidoacetates*, $[Pt(NH_2.CH_2.COO)Cl_2]R$, represented by the potassium salt.
(xii) *Dichloroamidopropionates*, $[Pt(NH_2.CH_3.CH.COO)Cl_2]R$, represented by the potassium salt.
(xiii) *Trichlorothiocarbamides*, $[Pt\{CS(NH_2)_2\}Cl_3]R$, represented by the acid, and the thiocarbamide salts.
(xiv) *Trichlorophosphotrianilides*, $[Pt\{P(C_6H_6N)_3\}Cl_3]R$, represented by the aniline salt.
(xv) *Trichlorophosphotritoluidides*, $[Pt\{P(C_7H_8N)_3\}Cl_3]$, represented by the toluidine salt.
(xvi) *Trichloroethylenes*, $[Pt(C_2H_4)Cl_3]R$, represented by (1) acid; (2) ammonium; (3) aniline; (4) ethylenediamine; (5) potassium; (6) silver; and (7) platinoustetrammine salts.
(xvii) *Trichlorocarbonyls*, $[Pt(CO)Cl_3]R$, represented by (1) amylamine; (2) aniline; (3) phenylhydrazine; (4) pyridine; and (5) quinoline.

(xviii) *Tribromocarbonyls*, $[Pt(CO)Br_3]R$, represented by the pyridine salt.

(xix) *Tri-iodocarbonyls*, $[Pt(CO)I_3]R$, represented by (1) potassium; and (2) trimethylamine salts.

(xx) *Trithiocyanatocarbonyls*, $[Pt(CO)(SCN)_3]R$, represented by (1) ammonium; and (2) potassium salts.

(xxi) *Trichloroallylalcohols*, $[Pt(C_3H_5OH)Cl_3]R$, represented by (1) cinchonine; (2) potassium; and (3) platinoustetrammine salts.

(xxii) *Tribromoallylalcohols*, $[Pt(C_3H_5OH)Br_3]R$, represented by (1) potassium; and (2) platinoustetrammine salts.

II.—*Platinous ammines with more than one platinum atom in the nucleus.*

(i) *Octammino-diol-sulphate*, $[Pt(NH_3)_4{=}(OH)_2{=}Pt(NH_3)_4]$.

III.—*The platinosic ammines—vide supra, platinum trichloride.*

IV.—*The platinic ammines with one platinum atom in the nucleus.*

1.—**The hexammine family,** or compounds of the quadrivalent group $[PtA_6)]''''$.

(i) *Ammines*, $[Pt(NH_3)_6]X_4$, represented by the (1) hydroxide; (2) chloride and chloroplatinate; (3) sulphate; (4) nitrate; (5) carbonate.

(ii) *Trispropylenediammines*, $[Pt(C_3H_6.N_2H_4)_3]X_4$, in its racemic, dextro- and lævo-forms, and represented by (1) chloride; (2) bromide; (3) iodide; (4) sulphate; (5) nitrate; and (6) tartrate.

2.—**The pentammine family,** or compounds of the tervalent group $[PtA_5X]X_3$.

(i) *Hydroxypentammines*, $[Pt(NH_3)_5(OH)]X_3$, represented by (1) chloride; (2) carbonate; (3) nitrate; and (4) acetate.

(ii) *Chloropentammines*, $[Pt(NH_3)_5Cl]X_3$, represented by the (1) hydroxide; (2) chloride, and the chloroplatinate; (3) sulphate and the chlorosulphate; (4) carbonate; and (5) nitrate.

(iii) *Bromopentammines*, $[Pt(NH_3)_5Br]X_3$, have been prepared.

(iv) *Chloroethylenediaminotriammines*, $[Pt(NH_3)_3\,enCl]X_3$, represented by the (1) chloride; (2) sulphate; and (3) nitrate.

3.—**The tetrammine family,** or compounds represented by the PtA_4-group.

A.—Type: $[PtA_4X_2]Y_2$, which has a bivalent group.

(i) *Dihydroxytetrammines*, $[Pt(NH_3)_4(OH)_2]Y_2$, represented by (1) chloride and chloroplatinate; (2) bromide; (3) iodide; (4) sulphate; (5) nitrite; (6) nitrate; and (7) dichromate.

(ii) *Dichlorotetrammines*, $[Pt(NH_3)_4Cl_2]Y_2$, represented by (1) chloride; chloroplatinite, and chloroplatinate; (2) bromide; (3) sulphate and sulphatoplatinate; (4) nitrate and nitratoplatinate; (5) carbonate; (6) oxalate; (7) thiocyanate; (8) chromate; and (9) dichromate.

(iii) *Dibromotetrammines*, $[Pt(NH_3)_4Br_2]Y_2$, represented by (1) chloride; (2) bromide; (3) sulphate and sulphatoplatinate; (4) nitrate and nitratoplatinate; (5) phosphate; (6) carbonate and carbonatoplatinate; (7) oxalate; and (8) dichromate.

(iv) *Chloroamidotetrammines*, $[Pt(NH_3)_4NH_2Cl]Y_2$, represented by (1) chloride; (2) bromide; and (3) nitrate.

(v) *Bromoamidotetrammines*, $[Pt(NH_3)_4NH_2Br]Y_2$, represented by the bromide.

(vi) *Chloronitritotetramminochloride*, $[Pt(NH_3)_4(NO_2)Cl]Cl_2$.

(vii) *Chloronitritopyridinotriamminochloride*, $[Pt(NH_3)_3\,py(NO_2)Cl]Cl_2$.

(viii) *Dichloroethylenediaminodiamminochloride*, $[Pt(NH_3)_2\,enCl_2]Cl_2$.

(ix) *Chloronitritoethylenediaminodiamminochloride*, $[Pt(NH_3)_2\,en(NO_2)Cl]$-Cl_2.

(x) *Dichloropyridinoethylenediaminoamminochloride*, $[Pt(NH_3)\,en\,pyCl_2]Cl_2$.

(xi) *Chloronitritopyridinoethylenediaminoamminochloride*, $[Pt(NH_3)\,en\,py$-$(NO_2)Cl]Cl_2$.

(xii) *Diiodotetrammines*, $[Pt(NH_3)_4I_2]X_2$, represented by (1) iodide and iodoplatinate; (2) sulphate; and (3) nitrate.

(xiii) *Sulphatotetrammines*, $[Pt(NH_3)_4SO_4]X_2$, represented by (1) hydroxide; (2) sulphate; (3) chlorosulphate; and (4) bromosulphate.

(xiv) *Dinitritotetrammines*, $[Pt(NH_3)_4(NO_2)_2]X_2$, represented by the nitrate.

(xv) *Dinitratotetrammines*, $[Pt(NH_3)_4(NO_3)_2]X_2$, represented by (1) chloride, and chloroplatinate; (2) nitrate; (3) carbonatoplatinate; (4) chromate; and (5) dichromate.

(xvi) *Carbonatotetrammines*, $[Pt(NH_3)_4CO_3]X_2$, represented by (1) carbonate; (2) chlorocarbonate; (3) bromocarbonate; and (4) nitratocarbonate.

(xvii) *Dichloroquatermethylamines*, $[Pt(CH_3NH_2)_4Cl_2]X_2$ represented by (1) chloride; and (2) nitrate.

(xviii) *Dichloroquaterethylamines*, $[Pt(C_2H_5NH_2)_4Cl_2]X_2$, represented by the chloride and chloroplatinite.

(xix) *Dichloroethylenediaminodiammines*, $[Pt\ en(NH_3)_2Cl_2]X_2$, represented by the chloride.

(xx) *Dichlorobisethylenediamines*, $[Pt\ en_2Cl_2]X_2$, represented by the chloride, chlorocuprates, and chloroplatinite.

(xxi) *Dibromobisethylenediamines*, $[Pt\ en_2Br_2]X_2$, represented by the bromide, bromocuprates, and bromoplatinite.

(xxii) *Dithiocyanatobisethylenediamines*, $[Pt\ en_2(CNS)_2]X_2$, represented by the thiocyanate.

(xxiii) *Dichlorobispropylenediamines*, $[Pt\ pn_2Cl_2]X_2$, represented by the chloride.

(xxiv) *Dibromobispropylenediamines*, $[Pt\ pn_2Br_2]X_2$, represented by the bromide.

(xxv) *Dichloroquaterpyridines*, $[Pt\ py_4Cl_2]X_2$, represented by the (1) chloride, chloroplatinite, and chloroplatinate; and (2) nitrate.

(xxvi) *Dibromoquaterpyridines*, $[Pt\ py_4Br_2]X_2$, represented by (1) nitrate; and (2) hydronitrate.

(xxvii) *Dichloroquatermethylpseudolutidostyril*, $[Pt(C_8H_{11}NO)_4Cl_2]X_2$, represented by the chloride.

(xxviii) *Hydroxychlorotetrammines*, $[Pt(NH_3)_4(OH)Cl]X_2$, represented by (1) chloride; (2) bromide; (3) nitrate; (4) carbonate; (5) oxalate; (6) chromate; and (7) dichromate.

(xxix) *Hydroxybromotetrammines*, $[Pt(NH_3)_4(OH)Br]X_2$, represented by (1) chloride; (2) bromide; (3) nitrate; and (4) oxalate.

(xxx) *Hydroxyiodotetrammines*, $[Pt(NH_3)_4(OH)I]X_2$, represented by the (1) iodoplatinate; and (2) sulphate.

(xxxi) *Hydroxynitratotetrammines*, $[Pt(NH_3)_4(OH)(NO_3)]X_2$, represented by (1) nitrate; (2) pyrophosphate; and (3) oxalate.

(xxxii) *Hydroxyacetatotetrammines*, $[Pt(NH_3)_4(OH)(C_2H_3O_2)]X_2$, represented by (1) chloride, and chloroplatinite; (2) sulphate; (3) nitrate; and (4) dichromate.

(xxxiii) *Chloroaminotetrammines*, $[Pt(NH_3)_4(NH_2)Cl]X_2$, represented by the (1) hydroxydihydrophosphate; and (2) the bisdihydrophosphate.

(xxxiv) *Nitritochloroethylenediaminodiammines*, $[Pt(NH_3)_2\ en(NO_2)Cl]X_2$, represented by the chloride.

(xxxv) *Nitratochlorotetrammines*, $[Pt(NH_3)_4(NO_3)Cl]X_2$, represented by (1) sulphate; and (2) nitrate.

(xxxvi) *Nitratobromotetrammines*, $[Pt(NH_3)_4(NO_3)Br]X_2$, represented by (1) sulphate; and (2) nitrate.

(xxxvii) *Chlorobromotetrammines*, $[Pt(NH_3)_4ClBr]X_2$, represented by the chloride.

(xxxviii) *Chloroiodotetrammines*, $[Pt(NH_3)_4ClI]X_2$, represented by the chloride.

(xxxix) *Nitratobromoquaterpyridines*, $[Pt\,py_4(NO_3)Br]X_2$, represented by the hydronitrate.

(xl) *Dibromopropylenediaminediammines*, $[Pt(NH_3)_2\,pn\,Br_2]X_2$, represented by the chloride.

(xli) *Diiodobispyridinediammines*, $[Pt(NH_3)_2\,py_2I_2]X_2$, represented by the iodide.

B.—Type : $[PtA_4X_3]Y$, which has a univalent group.

(i) *Phosphatotetrammines*, $[Pt(NH_3)_4(PO_4)]Y$, represented by (1) chloride ; (2) bromide ; and (3) nitrate.

(ii) *Hydroxysulphatotetrammines*, $[Pt(NH_3)_4(OH)(SO_4)]Y$, represented by (1) chloride and chloroplatinate ; (2) bromide ; (3) sulphate ; (4) nitrate ; (5) oxalate ; (6) chromate ; (7) dichromate.

(iii) *Chlorosulphatotetrammines*, $[Pt(NH_3)_4Cl(SO_4)]Y$, represented by sulphate.

(iv) *Bromosulphatotetrammines*, $[Pt(NH_3)_4Br(SO_4)]Y$, represented by the sulphate.

(v) *Chlorocarbonatotetrammines*, $[Pt(NH_3)_4Cl(CO_3)]Y$, represented by the chloronitratocarbonatoplatinate.

(vi) *Bromocarbonatotetrammines*, $[Pt(NH_3)_4Br(CO_3)]Y$, represented by (1) carbonate ; and (2) bromonitratocarbonatoplatinate.

(vii) *Nitratocarbonatoammines*, $[Pt(NH_3)_4(NO_3)(CO_3)]Y$, represented by the carbonate.

4.—**The triammine family** represented by the univalent group $[Pt(NH_3)_3X_3]$.

(i) *Trichlorotriammines*, $[Pt(NH_3)_3Cl_3]Y$, represented by the chloride.

(ii) *Nitritodichloroethylenediaminomethylamines*, $[Pt\,en(CH_3.NH_2)(NO_2)Cl_2]Y$, represented by the chloride.

(iii) *Dinitritochloroethylenediaminomethylamines*, $[Pt\,en(CH_3.NH_2)(NO_2)_2Cl]Y$, represented by the chloride.

(iv) *Dinitritochloroethylenediaminopyridines*, $[Pt\,en\,py(NO_2)_2Cl]Y$, represented by the chloride.

(v) *Dinitritochloroethylenediaminoammines*, $[Pt\,en(NH_3)(NO_2)_2Cl]Cl$, in cis- and trans-forms.

(vi) *Dichloronitritotriamminochloride*, $[Pt(NH_3)_3(NO_2)Cl_2]Cl$.

(vii) *Chlorodinitritotriamminochloride*, $[Pt(NH_3)_3(NO_2)_2Cl]Cl$.

(viii) *Chlorodinitritopyridinodiamminochloride*, $[Pt(NH_3)_2\,py(NO_2)_2Cl]Cl$.

(ix) *Dichloronitritopyridinodiamminochloride*, $[Pt(NH_3)_2\,py(NO_2)Cl_2]Cl$.

(x) *Dichloronitritopyridinomethylaminoamminochloride*, $[Pt(NH_3)(CH_3NH_2)py(NO_2)Cl_2]Cl$.

(xi) *Chlorodinitritopyridinomethylaminoamminochloride*, $[Pt(NH_3)(CH_3NH_2)py(NO_2)_2Cl]Cl$.

(xii) *Dichloronitritopyridinomethylaminoamminochloride*, $[Pt(NH_3)(CH_3NH_2)\,py(NO_2)Cl_2]Cl$, and isomerides.

(xiii) *Chlorodinitritopyridinoethylenediaminochloride*, $[Pt\,en\,py(NO_2)_2Cl]Cl$, and isomerides.

(xiv) *Trichloropyridinoethylenediaminochloride*, $[Pt\,en\,pyCl_3]Cl,2H_2O$.

(xv) *Trichloropyridineethylenediaminohydroxide*, $[Pt\,en\,pyCl_3]OH$.

(xvi) *Dichloronitroethylenediaminoamminochloride*, $[Pt(NH_3)\,en(NO_2)Cl_2]Cl$, and their isomerides.

(xvii) *Trichloroethylenediaminoamminochloride*, $[Pt(NH_3)\,enCl_3]Cl$.

(xviii) *Dichloronitritopyridinoethylenediaminochloride*, $[Pt\,en\,py(NO_2)Cl_2]Cl$.

(xix) *Chlorodinitritopyridinoethylenediaminochloride*, $[Pt\,en\,py(NO_2)_2Cl]Cl$.

(xx) *Chlorodinitritopyridinoethylenediaminohydroxide*, $[Ptenpy(NO_2)_2Cl]OH$.

(xxi) *Chloroamidonitritopyridinoethylenediaminochloride*, $[Pt\,en\,py(NH_2)(NO_2)Cl]Cl.2H_2O$.

(xxii) *Dichloronitritopyridinoethylenediaminochloride*, $[Pt\,en\,py(NO_2)Cl_2]Cl$, and its isomerides.

(xxiii) *Dichloronitritoethylenediaminoamminohydroxide*, $[Pt(NH_3)\,en(NO_2)Cl_2]$-OH, and its isomerides.

(xxiv) *Trichlorotristribenzyloxyphosphines*, $[Pt\{(C_7H_7)_3PO\}_3Cl_3]Y$, represented by the chloride.

(xxv) *Dihydroxynitratotriammines*, $[Pt(NH_3)_3(OH)_2(NO_3)]Y$, represented by the nitrate.

(xxvi) *Hydroxydinitratotriammines*, $[Pt(NH_3)_3(OH)(NO_3)_2]Y$, represented by the bromide.

(xxvii) *Dinitratochlorotriammines*, $[Pt(NH_3)_3Cl(NO_3)_2]Y$, represented by the chloride.

(xxviii) *Dinitratobromotriammines*, $[Pt(NH_3)_3Br(NO_3)_2]Y$, represented by the bromide.

(xxix) *Nitratodibromotriammines*, $[Pt(NH_3)_3Br_2(NO_3)]Y$, represented by the iodide.

(xxx) *Sulphatobromotriammines*, $[Pt(NH_3)_3Br(SO_4)]Y$, represented by the bromide.

5.—**The diammine family** represented by the null valent group $[Pt(NH_3)_2X_4]$.

(i) *Diammines*, $[Pt(NH_3)_2X_4]$, represented by the cis- and trans-forms of (1) hydroxide; (2) chloride; (3) bromide; (4) iodide; (5) polyiodide; (6) sulphate; (7) nitrate; and (8) cyanide. Also (1) trimethyliodide; (2) nitritotrichloride and a double salt with silver nitrite; (3) nitratotrichloride and a double salt with chloroplatinite; and (4) nitratotrihydroxide. Also the cis- and trans-forms of (1) dihydroxysulphate; (2) dihydroxydinitrate; (3) dihydroxyoxalate; (4) trichloronitrite; (5) dichlorodinitrite; (6) dibromodinitrite; (7) sulphatodinitrite; and (8) dinitritodinitrate. There are also (1) hydroxychlorodinitrite; and (2) chlorodinitritonitrate.

(ii) *Propylenediamines*, $[Pt\,pnX_4]$, represented by the chloride.

(iii) *Ethylenediamines*, $Pten(NO_2)Cl_2]$.

(iv) *Ethylenediamines*, $[Pt\,enX_4]$, represented by (1) trichloronitrite; (2) the amidotrichloride; (3) the amidonitritodichloride; and (4) the ethyleneaminoimidotrichloride.

(v) *αβ-isobutylenediamines*, $[Pt\{C_4H_8(NH_2)\}_2][Pt$ or $PdCl_4]$, etc.

(vi) *Bispyridines*, $[Pt\,py_2X_4]$, represented by cis- and trans-forms of (1) chloride; (2) bromide; (3) dibromodichloride; (4) iodide; and (5) sulphate.

(vii) *Pyridinoammines*, $[Pt(NH_3)\,pyX_4]$, represented by the trichloronitrite.

(viii) *Bispicolines*, $[Pt(C_6H_7N)_2X_4]$, represented by the chloride of α-, β-, and γ-picoline.

(ix) *Bislutidines*, $[Pt(C_7H_9N)_2X_4]$, represented by the chloride.

(x) *Biscollidines*, $[Pt(C_8H_{11}N)_2X_4]$, represented by the chloride.

(xi) *Bisquinolines*, $[Pt(C_9H_7N)_2X_4]$, represented by the chloride.

(xii) *Bistetrahydroquinolines*, $[Pt(C_9H_{11}N)_2X_4]$, represented by the chloride.

(xiii) 3-*methyl*-2-*aminomethyl*-4-*ethylquinolines*, $[Pt(C_{13}H_{14}N.NH_2)_2][PtCl_4]$.

(xiv) *Bispropionitriles*, $[Pt(C_2H_5CN)_2X_4]$, represented by the chloride.

(xv) *Bisbenzonitriles*, $[Pt(C_6H_5CN)_2X_4]$, represented by (1) chloride; and (2) bromide.

(xvi) *ββ-dimethyldipyridyls*, $[Pt(C_{12}H_{12}N_2)X_4]$, represented by the chloride.

(xvii) *Bis*-4, 5-*dimethylpyrimidines*, $[Pt(C_6H_8N_2)_2X_4]$, represented by the chloride.

(xviii) *Bis*-4, 5-*methylethylpyrimidines*, $[Pt(C_7H_{10}N_2)_2X_4]$, represented by the chloride.

(xix) *Bisjaborines*, $[Pt(C_9H_{14}N_2)_2X_4]$, represented by the chloride.

(xx) *Bis-α-methylisoxazols*, $[Pt(C_4H_5NO)_2X_4]$, represented by the chloride.

(xxi) *Bis-β-hydroxyethylpyridine*, $[Pt(C_7H_9NO)_2X_4]$, represented by the chloride.

(xxii) *Bisamidoacetates*, $[Pt(NH_2.CH_2.COOH)_2X_4]$, represented by (1) chloride; (2) bromide; (3) bromochloride; (4) iodide; and (5) iodobromide.

(xxiii) *Bisamidoethylacetates*, $[Pt(NH_2.CH.COOC_2H_5)_2X_4]$, represented by (1) chloride; and (2) bromochloride.

(xxiv) *Bis-β-pyridine-α-lacetates*, $[Pt(C_8H_9NO_3)_2X_4]$, represented by the chloride.

(xxv) *Bisjaborinates*, $[Pt(C_{19}H_{25}N_3O_5)_2X_4]$, represented by the chloride.

(xxvi) *Bistrichloropyridines*, $[Pt(C_5H_2Cl_3N)_2X_4]$, represented by the chloride.

(xxvii) *Bispyrazole*, $[Pt(C_3H_4N_2)_2X_4]$, represented by the chloride.

(xxviii) *Bis*-3, 5-*methylpyrazol*, $[Pt(C_4H_6N_2)_2X_4]$, represented by the chloride.

(xxix) *Bis*-3, 5-*methylchloropyrazol*, $[Pt(C_4H_5N_2Cl)_2X_4]$, represented by the chloride.

(xxx) *Bis*-3, 5-*dimethylpyrazole*, $[Pt(C_5H_8N_2)_2X_4]$, represented by the chloride.

(xxxi) *Bis*-3, 5-*dimethyltetrachloropyrazole*, $[Pt(C_5H_4N_2Cl_4)_2X_4]$, represented by the chloride.

(xxxii) *Bis-p-tolylpyrazole*, $[Pt(C_{10}H_{10}N_2)_2X_4]$, represented by the chloride.

(xxxiii) *Bisglyoxaline*, $[Pt(C_3H_4N_2)_2X_4]$, represented by the chloride.

(xxxiv) *Pyrazine*, $[Pt(C_4H_4N_2)X_4]$, represented by the chloride.

(xxxv) *Bis*-2, 5-*dimethylpyrazine*, $[Pt(C_6H_8N_2)_2X_4]$, represented by the chloride.

(xxxvi) 2, 5-*dimethyl*-3-*ethylpyrazine*, $[Pt(C_8H_{12}N_2)X_4]$, represented by the chloride.

(xxxvii) *Biscinnamenylpyridazine*, $[Pt(C_{12}H_{10}N_2)_2X_4]$, represented by the chloride.

(xxxviii) *Bis*-1, 3, 4-*triazole*, $[Pt(C_2H_3N_3)_2X_4]$, represented by the chloride.

(xxxix) *Bis*-1-*phenyltriazoles*, $[Pt(C_8H_7N_3)_2X_4]$, represented by the chlorides with 1, 3- and 2, 3-triazole.

(xl) *Bis*-1-*tolyltriazole*, $[Pt(C_9H_9N_3)_2X_4]$, represented by the chloride with 1, 3- and 2, 3-triazole, and *o*- and *p*-tolyl.

(xli) *Bis*-1-*naphthyltriazoles*, $[Pt(C_{12}H_9N_3)_2X_4]$, represented by the chlorides with 1, 3- and 2, 3-triazole, and α- and β-naphthyl.

(xlii) *Bis*-1-*phenyl*-3-*methyl*-1, 3-*triazole*, $[Pt(C_9H_9N_3)_2X_4]$, represented by the chloride.

(xliii) *Bis*-1-*tolyl*-2, 5-*dimethyl*-2, 3-*triazoles*, $[Pt(C_{11}H_{13}N_3)_2X_4]$, represented by the chlorides with *o*- and *p*-tolyl.

(xliv) *Bis*-1-*phenyl*-3-*imidotriazoline*, $[Pt(C_8H_8N_4)_2X_4]$, represented by the chloride.

(xlv) *Bis*-1-*tolyl*-3-*imidotriazoline*, $[Pt(C_9H_{10}N_4)_2X_4]$, represented by the chloride of *p*-tolyl.

(xlvi) *Bistetrazolines*, $[Pt(C_2H_4N_4)_2X_4]$, represented by the chloride.

(xlvii) *Bisdimethyltriazolines*, $[Pt(C_4H_8N_4)_2X_4]$, represented by the chlorides.

(xlviii) *Bisimidazolylmercaptan*, $[Pt(HS.C.NH.CH:CH.N:)_2X_4]$, represented by the chloride.

(xlix) *Bis-μ-imidazolylmercaptan*, $[Pt(HS.C.NH.CH:CH.N:)_2X_4]$, represented by the chloride.

(l) *Bis-ν-methylimidazolyl-μ-mercaptan*, $[Pt(HS.C.N(CH_3).CH:CH.N:)_2X_4]$, represented by the chloride.

(li) *Bis-ν-phenylimidazolyl-μ-mercaptan*, $[Pt(HS.C.N(C_6H_5).CH:CH.N:)_2X_4]$, represented by the chloride.

(lii) *Bis-ν-tolylimidazolyl-μ-mercaptan*, $[Pt(HS.C.N(C_7H_7).CH:CH.N:)_2X_4]$, represented by the chloride of *p*-tolyl.

(liii) *Bis-ν-xylylimidazolyl-μ-mercaptan*, $[Pt(HS.C.N(C_8H_9).CH:CH.N:)_2X_4]$, represented by the chloride.

(liv) *Bis-v-naphthylimidazolyl-μ-mercaptan,* $[Pt(HS.C.N(C_{10}H_7)CH:CH.N:)_2X_4]$, represented by the chloride of α-naphthyl.

(lv) *Bistrimethylenethiocarbamide,* $[Pt(HS.C:N(CH_2)_3NH)_2X_4]$, represented by the chloride.

(lvi) *Bisethylenethiocarbamide,* $[Pt(S:C.NH:C_2H_4:NH)_2X_4]$, represented by the chloride.

(lvii) *Bisethylalcohol,* $[Pt(C_2H_5OH)_2X_4]$, represented by the chloride. *s*

(lviii) *Bismethylsulphine,* $[Pt\{(CH_3)_2S\}_2X_4]$, represented by (1) chloride; (2) bromide; (3) bromochloride; (4) iodide; (5) chloroiodide; and (6) bromoiodide.

(lix) *Bisethylsulphines,* $[Pt\{(C_2H_5)_2S\}_2X_4]$, represented by (1) chloride; (2) bromide; (3) chlorobromide; and (4) iodide.

(lx) *Bismethylethylsulphine,* $[Pt\{(CH_3)(C_2H_5)S\}_2X_4]$, represented by the chloride.

(lxi) *Bispropylsulphines,* $[Pt\{(C_3H_7)_2S\}_2X_4]$, represented by normal and iso-salts: (1) chloride; (2) bromide; (3) chlorobromide; and (4) hydroxynitrate.

(lxii) *Bisbutylsulphines,* $[Pt\{(C_4H_9)_2S\}_2X_4]$, represented by secondary, normal, and iso-salts: (1) chloride; (2) bromide; (3) chlorobromide; (4) iodide; (5) polyiodide; and (6) chloroiodide.

(lxiii) *Bisbenzylsulphine,* $[Pt\{(C_6H_5.CH_2)_2S\}_2X_4]$, represented by the chloride.

(lxiv) *Ethylenedisulphine,* $[Pt\{(C_2H_4)_2S_2\}X_4]$, represented by the chloride.

(lxv) *Bistrithioformaldehyde,* $[Pt(C_3H_6S_3)_2X_4]$, represented by the chloride.

(lxvi) *Bismethylselenine,* $[Pt\{(CH_3)_2Se\}_2X_4]$, represented by the chloride.

(lxvii) *Bisethylselenines,* $[Pt\{(C_2H_5)_2Se\}_2X_4]$, represented by (1) chloride; (2) bromide; (3) chlorobromides; (4) iodide; (5) chloroiodides; (6) bromoiodides; (7) chloronitrite; (8) bromonitrite; (9) iodonitrite; (10) nitrate; (11) hydroxynitrate; (12) chloronitrate; and (13) bromonitrate.

(lxviii) *Bisbenzylselenines,* $[Pt\{(C_6H_5.CH_2)_2Se\}_2X_4]$, represented by the chloride.

(lxix) *Bisphosphorichlorides,* $[Pt(PCl_5)_2X_4]$, represented by the chloride.

(lxx) *Bisethylphosphines,* $[Pt\{P(C_2H_5)_3\}_2X_4]$, represented by the (1) dichlorodibromides; and (2) dichlorodiiodides.

(lxxi) *Bisethylphosphites,* $[Pt\{P(OC_2H_5)_3\}_2X_4]$, represented by (1) chloride; and (2) dichlorobromide.

(lxxii) *Bismethylphosphates,* $[Pt\{OP(OCH_3)_3\}_2X_4]$, represented by the bromide.

(lxxiii) *Bismethyloxyphosphinebenzoates,* $[Pt\{(CH_3)_2POC_6H_4COOH\}_2X_4]$, represented by the chloride.

(lxxiv) *Bisglycines,* $[Pt(NH_2.CH_2.COO)_2X_2]$, represented by (1) chloride; (2) bromide; and (3) iodide.

(lxxv) *Bismethylethylglyoximines,* $[Pt(NO:C.C_2H_5.CH_3.C:NOH)_2X_2]$, represented by the bromide.

(lxxvi) *Bispyrazoles,* $[Pt(C_3H_3N_2)_2X_2]$, represented by the chloride.

(lxxvii) *Bis-*3, 5*-methylpyrazoles,* $[Pt(C_4H_5N_2)_2X_2]$, represented by the chloride.

(lxxviii) *Bis-*3, 5*-dimethylpyrazoles,* $[Pt(C_5H_7N_2)_2X_2]$, represented by the chloride.

(lxxix) *Bis-*1*-ethyl-*3, 5*-dimethylpyrazoles,* $[Pt(C_7H_{11}N_2)_2X_2]$, represented by the chloride.

(lxxx) *Bis-*1*-phenylpyrazoles,* $[Pt(C_9H_7N_2)_2X_2]$, represented by the chloride.

(lxxxi) *Bis-*1*-phenyltetrachloropyrazols,* $[Pt(C_9H_3N_2Cl_4)_2X_2]$, represented by the chloride.

(lxxxii) *Bistolylpyrazols,* $[Pt(C_{10}H_9N_2)_2X_2]$, represented by the chlorides of *o*- and *p*-tolyl.

(lxxxiii) *Bis-1-phenylmethylpyrazoles*, $[Pt(C_{10}H_9N_2)_2X_2]$, represented by the 3-methyl and the 4-methyl chlorides.
(lxxxiv) *Bis-1-phenyl-3, 5-dimethylpyrazoles*, $[Pt(C_{11}H_{11}N_2)_2X_2]$, represented by the chloride.
(lxxxv) *Bisphenylmethylethylpyrazoles*, $[Pt(C_{12}H_{13}N_2)_2X_2]$, represented by the chloride.
(lxxxvi) *Bis-1-phenylmethylethyltrichloropyrazoles*, $[Pt(C_{12}H_{10}N_2Cl_3)_2X_2]$, represented by the chloride.
(lxxxvii) *Bispyridinephenylpyrazoles*, $[Pt(C_{12}H_7N_3)_2X_2]$, represented by the chloride.
(lxxxviii) *Bis-1-phenyl-3-methyl-1, 3-triazoles*, $[Pt(C_9H_8N_3)_2X_2]$, represented by the chloride.
(lxxxix) *Bis-1-phenyl-3-methyl-1, 3-triazolone*, $[Pt(C_9H_8ON_3)_2X_2]$, represented by the chloride.
(xc) *Pyridineammines*, $[Pt(NH_3)(C_5H_5N)X_4]$, represented by the chloride.
(xci) *Pyridinepiperidines*, $[Pt(C_5H_5N)(C_5H_{11}N)X_4]$, represented by the chloride.
(xcii) *Ethylsulphineethylselenine*, $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}X_4]$, represented by the (1) chloride; (2) bromide; (3) chlorobromide; (4) iodide; (5) bromoiodide; (6) bromonitrate; and (7) chloronitrate.

6.—**The monammine family** represented by compounds of:

A.—Type: $[PtAX_4]$ which is nullvalent.

(i) *Picoline*, $[Pt(C_6H_7N)X_4]$, represented by the chloride.
(ii) *o-Phenylenebisguanidide*, $[Pt(C_8H_9N_5)X_4]$, represented by the chloride.
(iii) *Pilocarpidine*, $[Pt(C_{10}H_{14}N_2O_2)X_4]$, represented by the chloride.
(iv) *Pilocarpine*, $[Pt(C_{11}H_{16}N_2O_2)X_4]$, represented by the chloride.
(v) *Jaborinate*, $[Pt(C_{19}H_{25}N_3O_5)X_4]$, represented by the chloride.
(vi) *Jaborine*, $[Pt(C_{22}H_{32}N_4O_4)X_4]$, represented by the chloride.
(vii) *Ethylsulphine*, $[Pt\{(C_2H_5)_2S\}X_4]$, represented by the chlorodibromoethylsulphide.
(viii) *Vinylsulphine*, $[Pt\{C_2H_3)_2S\}X_2]$, represented by the complex of the sulphide with the chloroplatinite.
(ix) *Allylsulphine*, $[Pt\{(C_3H_5)_2S\}X_2]$, represented by a complex of the sulphide with the chloroplatinite.
(x) *Diallylhexasulphine*, $[Pt\{(C_3H_5)_2S_6\}X_4]$, represented by the chloride.
(xi) *Phosphortrichloride*, $[Pt(PCl_3)X_4]$, represented by the chloride.
(xii) *Ethylphosphites*, $[Pt\{P(OC_2H_5)_3\}X_4]$, represented by (1) chloride; and (2) dichlorodibromide.
(xiii) *Methylphosphate*, $[Pt\{OP(OCH_3)_3\}X_4]_2$, represented by the dichlorodibromide.
(xiv) *Ethylphosphates*, $[Pt\{OP(OC_2H_5)_3\}X_4]_2$, represented by (1) chloride; and (2) dichlorodibromide.

B.—Type: $[PtAX_5]$ which is a univalent acidic radicle.

(i) *Pentachloroammines*, $[Pt(NH_3)Cl_5]R$, represented by (1) potassium; and (2) platinous tetrammine salts.
(ii) *Pentachloropyridines*, $[Pt(C_5H_5N)Cl_5]R$, represented by (1) pyridinium; (2) potassium; (3) rubidium; (4) cæsium; (5) lithium; (6) sodium; and (7) chloroplatinicquaterpyridine salts.
(iii) *Pentachloropicoline*, $[Pt(C_6H_7N)Cl_5]R$, represented by the picoline salt.
(iv) *Pentachlorolutidine*, $[Pt(C_7H_9N)Cl_5]R$, represented by the lutidine salt.
(v) *Pentachlorocollidine*, $[Pt(C_8H_{11}N)Cl_5]R$, represented by the collidine salt.
(vi) *Pentachloropyrazine*, $[Pt(C_4H_4N_2)Cl_5]R$, represented by the pyrazine salt.

(vii) *Pentachlorodimethylpyrazines*, $[Pt(C_6H_8N_2)Cl_5]R$, represented by the dimethylpyrazine salt.

(viii) *Pentachlorotrimethylpyrazines*, $[Pt(C_7H_{10}N_2)Cl_5]R$, represented by the trimethylpyrazine salt.

(ix) *Pentachloro-2, 5-dimethyl-3-ethylpyrazines*, $[Pt(C_8H_{12}N_2)Cl_5]R$, represented by the corresponding pyrazine salt.

(x) *Pentachloroguanines*, $[Pt(C_5H_5N_5O)Cl_5]R$, represented by the corresponding guanine salt.

V.—*The platinic ammines with more than one platinum atom in the nucleus.*

(i) *Dihydroxyhexammine-μ-diamines*, $[(HO)(NH_3)_3Pt(NH_2)_2Pt(NH_3)_3(OH)]X_4$, represented by the (1) chloride ; (2) sulphate ; (3) nitrate ; (4) phosphate ; and (5) dichromate.

(ii) *Dibromohexammine-μ-diamines*, $[Br(NH_3)_3Pt(NH_2)_2Pt(NH_3)_3Br]X_4$, represented by (1) chloride ; (2) sulphate ; and (3) nitrate.

(iii) *Diiodohexammine-μ-diamines*, $[I(NH_3)_3Pt(NH_2)_2Pt(NH_3)_3I]X_4$, represented by (1) iodide ; (2) sulphate ; (3) nitrate ; (4) phosphate ; and (5) oxalate.

(iv) *Dinitratohexammino-μ-diamines*, $[(NO_3)(NH_3)_3Pt(NII_2)_2Pt(NH_3)_3(NO_3)]X_4$, represented by the nitrate.

(v) *Dibromohexammine-μ-diimines*, $[Br(NH_3)_3Pt(NH)_2Pt(NH_3)_3Br]X_2$, represented by the nitrate.

(vi) *Diiodohexammine-μ-diimines*, $[I(NH_3)_3Pt(NH)_2Pt(NH_3)_3I]X_2$, represented by the (1) iodide ; (2) sulphatoplatinite ; and (3) nitrate.

(vii) *Dinitratohexammine-μ-diimines*, $[(NO_3)(NH_3)_3Pt(NH)_2Pt(NH_3)_3(NO_3)]X_2$, represented by the sulphatoplatinite.

(viii) *Dihydrazinooctocarbylamines*, $[(CH_3.NC)_4Pt\left\langle\begin{array}{c}NH.NH_2\\NH_2.NH\end{array}\right\rangle Pt(CH_3.NC)_4]X_2.nH_2O$, represented by (1) chloride ; (2) iodide ; (3) perchlorate ; and (4) azide.

(ix) *Dihydrazinooctoethylcarbylamines*, $[C_2H_5.NC)_4Pt\left\langle\begin{array}{c}NH.NH_2\\NH_2.NH\end{array}\right\rangle Pt(C_2H_5.NC)_4]X_2.nH_2O$, represented by (1) chloride and chloroplatinate ; (2) iodide ; (3) perchlorate ; and (4) nitrate.

(x) *Dihydrazinohydrochlorotetracarbylamines*, $(CH_3.NC)_4.Pt_2.2N_2H_3.2HCl.Cl_2$.

(xi) *Dihydrazinohydrochlorotetraethylcarbylamines*, $(C_2H_5.NC)_4.Pt_2.2N_2H_3.2HCl.Cl_2$

VI.—*The platinum ammines whose nature is unknown.*

(i) *Platinum dihydroxytetrahydrocarbonateheptammine*, $Pt(NH_3)_7(OH)_2(HCO_3)_4$, of B. Gerdes.

(ii) *Platinum triehlorotriammine*, $Pt(NH_3)_3Cl_3$, of E. Koefoed.

(iii) *Platinum tetrammine*, $Pt_2(NH_3)_4X_2$, of P. T. Cleve, C. W. Blomstrand, H. and A. Euler, and P. Klason, represented by (1) hydroxide ; (2) chloride ; (3) sulphate ; and (4) nitrate.

(iv) *Platinum tetrammine*, $Pt_2(NH_3)_4X_4$, represented by the chloride of P. T. Cleve.

(v) *Platinum dicarbonylbispyridines*, $Pt_2(CO)_2(C_5H_5N)_2X_2$, of F. Förster, represented by (1) chloride ; (2) chloropyridine ; and (3) bromide.

(vi) *Platinum enneaiodoctammine*, $Pt_4(NH_3)_8I_9$, of P. T. Cleve.

(vii) *Platinum hexaiodotetrammine*, $Pt_2(NH_3)_4I_6$, of P. T. Cleve.

(viii) *Platinum pentaiodotetrammine*, $Pt_2(NH_3)_4I_5$, of P. T. Cleve.

(ix) *Platinum hexachlorobispyridinediammine*, $Pt_2(NH_3)_2(C_5H_5N)_2Cl_6$, of S. M. Jörgensen.

(x) *Platinum hexabromobisethylaminediammine*, $Pt_2(NH_3)_2(C_2H_5NH_2)_2Br_6$, of S. M. Jörgensen.

(xi) *Platinous triscarbonyltetrachloride*, $2PtCl_2.3CO$, of P. Schützenberger, and A. J. F. da Silva.
(xii) *Platinous tetrachlorotristhioformaldehyde*, $2PtCl_2.3C_3H_6S_3$, of A. W. Hofmann.
(xiii) *Platinic tetrasulphotrisamylsulphide*, $2PtS_2.3(C_3H_5)_2S$, of T. Wertheim
(xiv) *Platinum decahydroxyammine*, $(OH)_5Pt(NH_3)Pt(OH)_5$, of J. Jacobsen.
(xv) *Platinum decahydroxypyridine*, $(OH)_5Pt(C_5H_5N)Pt(OH)_5$, of J. Jacobsen.
(xvi) $Pt(NH_3)_4X_2NO.HX$, represented by the (1) chloride; (2) sulphatochloride; and (3) nitrate of E. Koefoed, and E. A. Hadow.
(xvii) $[Pt(NH_3)_4Cl_2]_2Cl_2(NO)(HCl)$, of E. Koefoed.
(xviii) $Pt(NH_3)_2(NO_2)(NO)Cl.HCl$, of E. Koefoed.
(xix) $Pt(NH_3)_2(NO_2)Cl(NO)(HNO_3)$, of E. Koefoed.
(xx) $Pt_2(NH_3)_4(NO)_2(OH)(HI)_2I_3$, of E. Koefoed.
(xxi) $Pt(NH_3)_2(NO_2)(NO)HCl$, of E. Koefoed.
(xxii) $Pt_2(NH_3)_6(HSO_4)_2SO_4(NO)_2(H_2SO_4)(HCl)$, of E. Koefoed.
(xxiii) $Pt\{(CH_3)_2NH\}_2(NO_2)_2(NO)(HCl)$, of E. Koefoed.
(xxiv) $Pt(NH_3)_2\{(CH_3)_2NH\}_2Cl_2(NO)[Pt(NH_3)_2\{(CH_3)_2NH\}_2Cl_2]Cl_2$, of E. Koefoed.
(xxv) $Pt_2(C_2H_5NH_2)_8(NO_2)Cl_3(NO)_2(HCl)_2.2H_2O$, of E. Koefoed.
(xxvi) $Pt(C_2H_5NH_2)_2(OH)Cl(NO)(HCl)$, of E. Koefoed.
(xxvii) $Pt(NH_3)_2(C_2H_5NH_2)_2Cl_2(NO)(HCl).2\frac{1}{2}H_2O$, of E. Koefoed.
(xxviii) $Pt(NH_3)_2(C_5H_5N)_2Cl_2(NO)(HCl).H_2O$, of E. Koefoed.
(xxix) $Pt(NH_3)(C_5H_5N)Cl_2(NO)(HNO_3).H_2O$, of E. Koefoed.
(xxx) $Pt\{(C_2H_5)_2S\}_2(NO_2)_2(NO)(HCl).[Pt\{(C_2H_5)_2S\}_2Cl_2]_2$, of E. Koefoed.
(xxxi) $(NH_4)HPtCl_2.H_2O$, of P. Schützenberger and C. Fontaine.
(xxxii) $Pt(PC_4H_{16}O_3N_2)Cl$, of P. Schützenberger and C. Fontaine.
(xxxiii) $Pt(OH)(OC_2H_5)_2.Pt.N_2H_4.2HCl.PtCl_4$, of P. Schützenberger and C. Fontaine.
(xxxiv) $Pt_2(NH_3)(N_2H_4)(P_2O_2)(C_2H_5O)_4$, of P. Schützenberger and C. Fontaine.
(xxxv) $P(OC_2H_5)_3Pt$, of P. Schützenberger.
(xxxvi) $P_2(OC_2H_5)_6Pt$, of P. Schützenberger.
(xxxvii) $Pt_3\{P(OC_2H_5)_3\}_2$, of P. Schützenberger and C. Fontaine.
(xxxviii) $Pt\{PO(OC_2H_5)_3\}$, of P. Schützenberger and C. Fontaine.
(xxxix) $Pt(NH_3)\{P_2O(OC_2H_5)_5\}Cl$, of P. Schützenberger and C. Fontaine.
(xl) $Pt(N_2H_4)P(OH)(OC_5H_{11})_2(HCl)$, of P. Schützenberger and C. Fontaine.

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§ 24. Platinous Bromide

W. Pullinger [1] could not prepare **platinous bromide**, or **platinum dibromide**, $PtBr_2$, by the direct action of bromine on platinum. V. Meyer and H. Züblin observed that in preparing platinic bromide by the action of bromine and hydrobromic acid on spongy platinum in a sealed tube, at 180°, evaporating the filtered soln., heating the residue to 180°, and extracting the platinic bromide from the

mass by water, a little platinous bromide remains undissolved. L. Wöhler and F. Müller obtained the anhydrous tetrabromide by heating bromoplatinic acid in a current of bromine at 300°; at 370° the tribromide is formed, and at 405° to 410°, the dibromide. The dibromide is thus difficult to prepare because it is stable over a temp. range of 5°. A. Gutbier observed that platinous bromide is formed when platinic bromide is heated to 180°; and W. Halberstadt, and H. Töpsöe, when hydrobromoplatinic acid is heated to 100°, or more rapidly at 200°. W. Halberstadt observed that the bromide is formed in the electrolysis of a conc. soln. of platinic bromide; and M. Katayama, during the working of the cell: $Pb|PbBr_{solid}|Br$ (and platinum).

W. Pullinger observed that platinous bromide is black if it has not been heated over 180°, and dark brown if prepared at 250°. W. Halberstadt, and H. Töpsöe said that the bromide forms a greenish-brown powder. R. Klement gave 6·652 for the sp. gr. at 25°/4°, and 53·4 for the mol. vol. H. Töpsöe showed that platinous bromide does not lose weight at 100°, but if heated at 200° for a long time a small proportion is decomposed, and if heated for a short time at 240° no decomposition can be detected. The salt is insoluble in water; it forms a brownish-red soln. with bromine water; and a yellow liquid with a soln. of potassium bromide. J. Thomsen gave (Pt, O, 4HBr, Aq.)=43·44 Cals. for the heat of formation of hydrobromoplatinous acid, H_2PtBr_4. W. Manchot and G. Lehmann observed that the halogen is eliminated more quickly in a current of carbon monoxide better than it is in an indifferent gas, and no carbonyl bromide is formed. W. Rosenheim and W. Levy described a complex with phosphorous bromide, namely, **platinous dibromobisphosphorotribromide,** $[Pt(PBr_3)_2Br_2]$; and also **platinous dibromophosphorotribromide,** $[Pt(PBr_3)Br_2]_2$.

J. Reiset obtained **platinous tetramminobromide,** $[Pt(NH_3)_4]Br_2.nH_2O$, by the action of barium bromide on a soln. of the tetramminosulphate. The cubic crystals are not decomposed by boiling water; and P. T. Cleve added that if the mixed soln. is evaporated over sulphuric acid, and the crystals are pressed between bibulous paper, four-sided prisms or plates of the *hemitrihydrate* are formed. The crystals effloresce in dry air; they lose water at 100°; and they dissolve freely in water. C. Nogareda, and A. A. Grinberg and B. V. Ptitsin studied the thermal decomposition, and formation of the bromide from its elements. E. Biilmann and A. C. Anderson prepared green **platinous tetramminobromoplatinate,** $[Pt(NH_3)_4]PtBr_4$, sparingly soluble in water; and they also obtained a complex platinous allylalcoholtetramminobromoplatinite, $[Pt(NH_3)_4][Pt(C_3H_5OH)Br_3]_2$. L. A. Tschugaeff and I. I. Tscherniaeff prepared **platinous aquotriamminobromoplatinite,** $[Pt(NH_3)_3(H_2O)]PtBr_4$, by adding potassium bromoplatinite to a soln. of the chloride. The green needles are converted by hydrobromic acid or a soluble bromide into **platinous bromotriamminobromoplatinite,** $[Pt(NH_3)_3Br]_2PtBr_4$. L. A. Tschugaeff prepared this salt by the method employed for the corresponding chloro-salt. P. T. Cleve prepared **platinous trans-dibromodiammine,** $[Pt(NH_3)_2Br_2]$, by the action of potassium bromide on the corresponding chloride, and drying the product at 100°. The pale yellow, crystalline powder is sparingly soluble in hot water, and the soln. on cooling deposits the original salt; he also obtained in an analogous manner, **platinous cis-dibromodiammine** in golden-yellow needles. H. D. K. Drew and co-workers prepared the three isomerides of **platinous dibromodiammine,** $[Pt(NH_3)_2Br_2]$, analogous with the corresponding chlorides (*q.v.*), by the action of an excess of a soln. of alkali bromide on the corresponding chloride, or of hydrobromic acid on the corresponding base. The *α-salt* forms sulphur-yellow, prismatic needles, which give no coloration with phenoxtellurine dibisulphate; a *β-salt* forms orange needles which give an orange-yellow coloration with phenoxtellurine dibisulphate; and the *γ-salt* occurs in clusters of dark orange prisms. H. Alexander prepared **platinous tetrahydroxylaminebromide,** $[Pt(NH_2OH)_4]Br_2$, in colourless needles, by the action of hydrobromic acid on the corresponding chloride.

S. M. Jörgensen prepared **platinous trans-dibromobismethylamine,** $[Pt(CH_3NH_2)_2Br_2]$, by evaporating on a water-bath, a soln. of platinous quatermethylaminechloroplatinite in aq. methylamine with repeated additions of conc. hydrobromic acid, washing with very dil. hydrobromic acid and then with alcohol, recrystallizing from boiling water, and drying at 100°. The yellow prisms are sparingly soluble in water and more soluble in alcohol. S. M. Jörgensen also prepared **platinous dibromobisdimethylamine,** $[Pt\{(CH_3)_2NH\}_2Br_2]$, as well as **platinous dibromobisdimethylaminediammine,** $[Pt(NH_3)_2\{(CH_3)_2NH\}_2]Br_2$, and **platinous dibromodimethylamineammine,** $[Pt(NH_3)\{(CH_3)_2NH\}Br_2]$. F. G. Mann prepared **platinous bromodiaminodiethylaminobromide,** $[BrPt(H_2N.C_2H_4)_2NH]Br$. H. Wolfram, H. Reihlen and E. Flohr, and A. Johnsen obtained golden-yellow **platinous quaterethylaminebromide,** $[Pt(C_2H_5NH_2)_4]Br_2$, and S. M. Jörgensen, **platinous cis-dibromobisethylamine,** $[Pt(C_2H_5NH_2)_2Br_2]$, **dibromoethylamineammine,** $[Pt(NH_3)(C_2H_3NH_2)Br_2]$. F. G. Mann prepared **platinous bis-β-methyltrimethylenediaminobromide,** $[Pt\{CH(CH_3)(CH_2.NH_2)_2\}_2]Br_2$; and **platinous bis-αβγ-triaminopropanobromide,** $[Pt\{NH_2.CH_2.CH(NH_2).CH_2.NH_2\}_2Br_2]$. P. C. Ray and co-workers prepared $PtBr(C_2H_5)_2S_2$; $Pt_2Br_2(C_2H_5)_2S_2.2py$; and $Pt_2Br_2.2(C_2H_5)_2S_2.2py$. H. Wolfram, and A. Johnsen obtained **platinum bisetbylaminediamminehexabromide,** $Pt_2(NH_3)_2(C_2H_5NH_2)_2Br_5$, of unknown constitution. N. S. Kurnakoff describod the complex **platinous bisethylenediaminebromocuprate,** [Pt en_2]$CuBr_4$; A. Werner, **platinous bispropylenediaminebromide,** $[Pt\{C_3H_6(NH_2)_2\}_2]X_2$; F. Förster, and P. C. Ray and N. N. Ghosh, **platinous quaterpyridinebromide,** $[Pt(C_5H_5N)_4]Br_2$, as a *trihydrate,* and S. G. Hedin, as a *pentahydrate;* F. Förster, and S. G. Hedin, **platinous cis-dibromobispyridine,** $[Pt(C_5H_5N)_2Br_2]$, and also **platinous trans-dibromobispyridine**; F. Förster, **platinous dibromocarbonylpyridine,** $[Pt(C_5H_3N)(CO)Br_2]$; W. Pullinger, and F. Mylius and F. Förster, **platinous dibromocarbonyl,** $[Pt(CO)X_2]_2$; F. Förster, **platinum dibromodicarbonylbispyridine,** $Pt_2(CO)_2(C_5H_5N)_2Br_2$, of unknown constitution; F. Mylius and F. Förster, **pyridinium carbonyltribromoplatinite,** $[Pt(CO)Br_3]H(C_5H_5N)$; L. Ramberg, **platinous dibromobisbenzonitrile,** $[Pt(C_5H_3.NC)_2Br_2]$, a complex with chloroform, and **platinous dibromobisphenylearbylamine,** $[Pt(C_5H_5.CN)_2Br_2]$; G. Wallin, **platinous dibromobisamidoacetate,** $[Pt(NH_2.CH_2.COOH)_2Br_2]$; and **platinous dibromobisethylamidoacetate,** $[Pt(NH_2.CH_2.COOC_2H_3)_2Br_2]$; E. Biilmann and A. C. Anderson described **potassium allylalcoholtribromoplatinite,** $K[Pt(C_3H_5OH)Br_3]$, as well as **platinous allylaleoholdiamminobromide,** $Pt(C_3H_5.OH)_2(NH_3)_2Br_5$.

L. Tschugaeff and D. Fränkel described **platinous quatermethylsulphinebromoplatinite,** $[Pt\{(CH_2)_2S\}_4]PtBr_4$; C. Enebuske, and L. Tschugaeff and D. Fränkel, **platinous dibromobismethylsulphine,** $[Pt\{(CH_3)_2S\}_2Br_2]$; C. W. Blomstrand, and P. Klason, **platinous dibromobisethylsulphine,** $[Pt\{(C_2H_5)_2S\}Br_2]$; M. Weibull, and C. Rudelius, **platinous dibromobispropylsulphine,** $[Pt\{(C_3H_7)_2S\}_2Br_2]$—with normal and iso-propyl; C. Rudelius, **platinous dibromoethylpropylsulphine,** $[Pt\{(C_2H_3)_2S\}\{(C_3H_7)_3S\}Br_2]$; M. Weibull, and H. Löndahl, **platinous dibromobisbutylsulphine,** $[Pt\{(C_4H_9)_2S\}Br_2]$, with normal, iso-, and secondary butyl; H. Löndahl, and C. W. Blomstrand, **platinous bisbenzylsulphine,** $[Pt\{(C_6H_5.CH_2)_2S\}_2Br_2]$, and complexes with alcohol, and with chloroform. H. Löndahl, and F. G. Angell and co-workers, **platinous bisethylenesulphinebromide,** $[Pt\{(C_2H_4)S\}_2]Br_2$, and **platinous dibromoethylenesulphine,** $[Pt\{(C_2H_4)S\}Br_2]$. K. A. Jensen measured the dipole moments, and the electrical conductivities of solutions of the salts—*vide* the chlorides.

N. S. Kurnakoff prepared **platinous quaterthiocarbamidebromide,** $[Pt\{CS(NH_2)_2\}_4]Br_2$, L. Tschugaeff and P. Teearu, and L. Ramberg, **platinous quaterphenylcarbylaminebromoplatinite,** $[Pt(C_5H_3.NC)_4]PtBr_4$; L. Tschugaeff and D. Fränkel, **platinous bisdiethylthioethylenoglycolbromoplatinite,** $[Pt(C_2H_5.S.C_2H_4.S.C_2H_5)_2]PtBr_4$; S. Tyden, **platinous dibromobisthiodiglycolate,** $[Pt\{S(CH_2.COOH)_2\}_2Br_2]$, and the corresponding **platinous dibromobispotassiumthioglycolate,** $[Pt\{S(CH_2.COOK)_2\}_2Br_2]$; S. Tyden, **platinous bromobisthiodiglycolate,** $[Pt\{S(CH_2.COOH)_2(HO.CO.CH_2.S.CH_2.COO)\}Br]$, **platinous bromobispotassiumthioglyoolate,** $[Pt\{S(CH_2.COOK)_2(KO.CO.CH_2.S.COO)\}Br]$, **platinous bromobisbariumthioglyoolate**; J. Petren, **platinous dibromoethylselenine,** $[Pt\{(C_2H_5)_3Se\}_2Br_2]$, also **platinous dibromoethylseleninebromoplatinite,** $[Pt\{(C_2H_5)_2Se\}_2Br_2]PtBr_2$, **platinous dibromoethylseleninepyridine,** $[Pt\{C_2H_5)_2Se\}(C_5H_5N)Br_2]$, and **platinous dibromoethylsulphineethylselenine,** $[Pt\{(C_2H_5)_2S\}\{(C_2H_3)_2Se\}Br_2]$. A. Rosenheim and W. Levy, **platinous dibromobisphosphorotribromide,** $[Pt(PBr_3)_2Br_2]$; K. A. Jensen, cis- and trans-**platinous dibromobistriethylphosphine,** $[Pt\{(C_2H_5)_3P\}_2Br_2]$. A. Rosenheim and co-workers, **platinous dibromobismethylphosphite,** $[Pt\{P(OC.H_3)_3\}_2Br_2]$; **platinous dibromoethylphosphite,** $[PtBr_2.P(OC.H_3)_2]_2$; **platinous cis-dibromoanilinetriethylphosphite,** $[Pt(C_2H_3NH_2)\{P(OC_2H_3)_3\}Br_2]$; **platinous trans-dibromoanilinetriethylphosphite**; **platinous dibromophosphorobromide,** $[Pt(PBr_3)Br_2]$, and **platinous dibromotriethylphosphite,** $[Pt\{P(OC_2H_3)_3\}Br_2]$; and R. Bunsen, **platinous dibromo-oxycacodyl,** $[Pt\{As_2(CH_3)_4O\}Br_2]$.

G. Méker obtained octahedral crystals of **ammonium bromoplatinite** by the action of fused ammonium sulphate and ammonium or potassium bromide on finely-divided platinum. J. Thomsen also prepared sodium bromoplatinite, $Na_2PtBr_4.6H_2O$, by evaporating to dryness a soln. of platinic chloride in hydro-

bromic acid, and crystallizing from the aq. soln. of the residue. The heat of formation is (Pt, Br_2, $2NH_4Br$, Aq.)=31·84 Cals. J. Thomsen obtained **potassium bromoplatinite,** $K_2PtBr_4.2H_2O$, by boiling a soln. of a mol. of potassium chloroplatinite with 4 mols. of sodium bromide in so little water that a large proportion of the sodium chloride which is formed separates out. By repeated evaporation, filtering, and cooling, the potassium salt can be freed from most of the sodium chloride, and the salt can then be re-crystallized from its aq. soln. E. Biilmann and A. C. Anderson obtained it by evaporating on a water-bath a mixture of 115·5 grms. of hydrobromoplatinic acid with four times its weight of water with 28·3 grms. of potassium oxalate until the weight is about 218 grms. Allow the liquid to cool overnight, separate the product by suction, and dry it in air—yield 44 grms. N. Demassieux and J. Heyrovsky studied the dissociation of the salt in soln.

The prismatic crystals of the *dihydrate* are almost black, and, according to O. B. Böggild, they are rhombic bipyramids with the axial ratios $a:b:c$ =0·6058 : 1 : 0·7050. The optical character is negative. R. Klement gave 3·747 for the sp. gr. at 25°/4°, and 167·9 for the mol. vol. The crystals remain bright in a cool place, or in a closed vessel at ordinary temp. The water is given off when the crystals are exposed to sunlight, or kept in a desiccator. When the dihydrated crystals are allowed to stand over water, the vapour is absorbed and a dark red soln. is formed. The heat of formation of the anhydrous salt was found by J. Thomsen to be (Pt, Br_2, 2KBr)=32·31 Cals. ; (Pt, Br_2, 2KBr, Aq.=31·84 Cals. ; and the heat of solution, −10·63 Cals. E. Biilmann and A. C. Anderson observed that the salt is freely soluble in water, and when the soln. is boiled for some time, it is decomposed.

L. Wöhler and F. Müller prepared **platinum tribromide,** $PtBr_3$, by heating the tetrabromide at 370° ; at 405°, it decomposes into the dibromide. R. Klement obtained platinum tribromide analogous with the trichloride, and found its sp. gr. at 22°/4° to be 6·504, and its mol. vol. 66·9.

A. J. Balard, and P. A. von Bonsdorff dissolved platinum in a mixture of hydrobromic and nitric acids, evaporated the soln. at about 70°, and obtained **platinum tetrabromide,** or **platinic bromide,** $PtBr_4$. H. Töpsöe added that if the nitric acid is in excess some tetrabromonitrosylbromide is formed, and if the hydrobromic acid is in excess, hydrobromoplatinic acid. C. F. Rammelsberg observed that some platinic bromide is formed when a soln. of platinic sulphate is treated with barium bromate (bromide ?), and the filtered soln. evaporated. L. Pigeon employed a process analogous to that used in the preparation of platinic chloride. V. Meyer and H. Züblin employed the process indicated in connection with platinous bromide. W. Halberstadt evaporated to dryness the soln. of hydrobromoplatinic acid, obtained in V. Meyer and H. Züblin's process, in order to drive off the excess of bromine, extracted the mass with water, evaporated the soln. again to dryness, and then heated the brownish-red product to 180° to 200° with vigorous stirring until the vapour of hydrogen bromide was no longer perceptible. The product is boiled with water, and the soln. evaporated to dryness ; the residue is again heated to 180° and the sequence of operations repeated so that finally the filtered soln. is evaporated. L. von Müller observed that the nature of the product depends on the time occupied in drying the mass, and A. Gutbier and co-workers observed that the product is impure, and L. von Müller, and A. Gutbier and co-workers recommended drying the product in bromine at 180°. The product dried at different temp. contained the following percentage proportions of platinum :

	100°	110°	120°	120° to 130°
Platinum .	26·75	27.59	31·13 to 32·96	33·05 to 34·12 per cent.
	130° to 140°	140° to 150°	150° to 175°	180°
Platinum .	36·59 to 37·89	37·14	39·19 to 40·31	41·34 per cent.

L. Wöhler and F. Müller obtained the anhydrous tetrabromide by heating hydrobromoplatinic acid in a current of bromine at 300°. C. Nogareda studied the

formation of the bromide from platinum and found the stages are Pt→$PtBr$→$PtBr_4$. Platinic bromide was analyzed by V. Meyer and H. Züblin, W. Halberstadt, A. Gutbier and co-workers, L. von Müller, and A. Miolati and I. Bellucci. Dark brown, amorphous platinic bromide is stable in air. W. Peters observed that when it is dried in vacuo, it is somewhat moist. W. Halberstadt could not obtain it in the crystalline state, but C. F. Rammelsberg did do so. R. Klement gave 5·687 for the sp. gr. at 25°/4°, and 90·6 for the mol. vol. W. Pullinger found that after 4 hrs.' heating at 310°, in a current of air, the salt was not completely converted into platinous bromide and bromine. L. Wöhler and F. Müller's observations on the range of stability of the bromides are summarized in Fig. 90. C. Nogareda studied the subject. L. Pigeon said that the heat of formation of the solid is (Pt, $2Br_2$)=42·43 to 56·83 Cals. according as the bromine is liquid or gas; the heat of formation of the salt in soln., (Pt, $2Br_{2aq.}$, H_2O)=52·29 Cals.; and the heat of soln. is +9·86 Cals. A. Gutbier and co-workers said that hydrogen reduces platinic bromide, even at ordinary temp., forming hydrogen bromide. The salt is soluble in water, and L. Pigeon said that 100 c.c. of water dissolve 0·4 grm. of the salt at ordinary temp., and W. Halberstadt gave 0·41 grm. per 100 grms. of water at 20°. For the electrical conductivity, *vide infra*, dihydroxy-tetrabromoplatinic acid. According to W. Halberstadt, the salt is freely soluble in hydrobromic acid; and soln. of potassium, sodium, or calcium bromides give red precipitates.

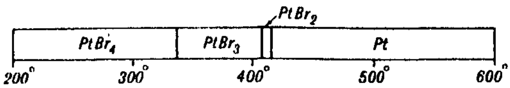

FIG. 90.—Range of Stability of the Platinum Bromides.

An aq. soln. of the salt was found by W. Halberstadt to give a fawn-coloured precipitate when treated with aq. ammonia, and a soln. of ammonium bromide gives a red precipitate. According to W. Peters, the anhydrous salt rapidly absorbs dry ammonia to form **platinic hexamminobromide,** $[Pt(NH_3)_6]Br_4$, and this, in vacuo, yields **platinic pentamminobromide,** $PtBr_4.5NH_3$. P. T. Cleve prepared **platinic dibromotetramminobromide,** $[Pt(NH_3)_4Br_2]Br_2$, by mixing hot soln. of the corresponding nitrate, and ammonium bromide; and A. Werner, by the action of bromine on a warm soln. of platinous tetramminosulphate. The orange-red crystals are sparingly soluble in hot water. Silver nitrate precipitates silver bromide from the aq. soln.—the hot filtered liquor on cooling furnishes pale yellow crystals of what is considered to be $[Pt(NH_3)_4(OH)Br](NO_3)_2$. L. A. Tschugaeff prepared **platinic bromoamidotetramminobromide,** $[Pt(NH_3)_4(NH_2)Br]Br_2$; and **platinic chloroamidotetramminobromide,** $[Pt(NH_3)_4(NH_2)Cl]Br_2$. P. T. Cleve obtained **platinic trans-tetrabromodiammine,** $[Pt(NH_3)_2Br_4]$, by adding bromine to platinous trans-chlorodiammine. The orange-yellow powder consists of four-sided plates, or octahedra, which are sparingly soluble in water. The corresponding **platinic cis-tetrabromodiammine** forms dark red prisms or rhombic or hexagonal plates, sparingly soluble in cold water. A. R. Klien studied the action of water, acids, and alkaline soln. According to E. G. Cox and G. H. Preston, the α- and β-diamminotetrabromides are isomorphous with the corresponding tetrachlorides.

H. Töpsöe prepared **platinic tetrabromonitrosylbromide,** $PtBr_4.2NOBr$, by dissolving platinum in a mixture of hydrobromic acid and an excess of nitric acid. The dark brown powder contains cubic crystals. Moisture decomposes the salt with the evolution of nitrous fumes; and when confined over calcium chloride nitrosyl bromide is evolved. P. T. Cleve obtained **platinic hydroxybromotetramminonitrate,** $[Pt(NH_3)_4(OH)Br](NO_3)_2$, by the action of silver nitrate on platinous dibromotetramminonitrate. The straw-yellow powder consists of short prisms. The salt loses nothing at 100°, but detonates like gunpowder when strongly heated. It is sparingly soluble in cold water, and freely soluble in hot water; hydrochloric acid converts it into chlorobromotetramminochloride; nitric acid forms bromonitratotetramminonitrate; and an excess of oxalic acid gives a mixed precipitate.

W. Manchot and G. Lehmann observed that in carbon monoxide the halogen

is eliminated at a lower temp. than it is in an indifferent gas, and that no carbonyl bromide is formed. W. Halberstadt and others observed that platinic bromide is easily soluble in absolute and in aq. alcohol, in alcohol, and in glycerol. The ethereal soln. deposits platinum when warmed ; the salt is also slightly soluble in acetic acid, and also in soln. of potassium or ammonium oxalate. An excess of soda-lye added to an aq. soln. of platinic chloride gives a yellowish-red precipitate, and silver nitrate, a brownish-red precipitate.

A. Gutbier and F. Bauriedel, F. Bauriedel, and P. Groth described **platinic bismethylaminehydrobromide**, $2CH_3NH_2.2HBr.PtBr_4$; A. Gutbier and F. Bauriedel, F. Bauriedel, A. Ries, T. Hjortdahl, and H. Töpsöe, **platinic bisdimethylaminehydrobromide**, $2(CH_3)_2NH.HBr.PtBr_2$; F. Bauriedel, A. Gutbier and F. Bauriedel, A. Ries, and H. Topsöe, **platinic bistrimethylaminehydrobromide**, $2(CH_3)_3N.HBr.PtBr_4$; A. Gutbier and A. Rausch, A. Ries, and H. Töpsöe, **platinic bistetramethylammonium bromide**, $2(CH_3)_4NH_3Br.PtBr_4$; F. Bauriedel, A. Gutbier and F. Bauriedel, H. Töpsöe, and P. Groth, **platinic bisethylaminehydrobromide**, $2C_2H_5NH_2.HBr.PtBr_4$; F. Bauriedel, A. Gutbier and F. Bauriedel, P. Groth, A. Ries, and H. Töpsöe, **platinic bisdiethylaminehydrobromide**, $2(C_2H_5)_2NH.HBr.PtBr_4$; H. D. K. Drew and H. J. Tress, **platinic quaterethylaminobromide**, $[Pt\,etn_4Br_2]Br_2$; F. Bauriedel, A. Gutbier and F. Bauriedel, H. Töpsöe, and P. Groth, **platinic bistriethylaminehydrobromide**, $2(C_2H_5)_3N.HBr.PtBr_4$; A. Gutbier and A. Rausch, and A. Rios, **platinic bistetraethylammoniumbromide**, $2(C_2H_5)_4NBr.PtBr_4$; J. A. le Bel, **platinic dimethyldiethylaminehydrobromide**, $(CH_3)_2NH.HBr.(C_2H_5)_2NH.HBr.PtBr_4$; A. Ries, **platinic bistrimethylethylammoniumbromide**, $2(CH_3)_3(C_2H_5)NBr.PtBr_4$; A. Ries, **platinic bisdimethyldiethylammoniumbromide**, $2(CH_3)_2(C_2H_5)_2NBr.PtBr_4$; A. Ries, **platinic bismethyltriethylammoniumbromide**, $2(CH_3)(C_2H_5)_3NBr.PtBr_4$; F. Bauriedel, and A. Gutbier and F. Bauriedel, **platinic bis-n-propylaminehydrobromide**, $2C_3H_7NH_2.HBr.PtBr_4$, and also **platinic bis-i-propylaminehydrochloride** ; J. A. le Bel, A. Ries, and P. Groth, **platinic bispropylaminehydrobromide**, $2(C_3H_7)_2NH.HBr.PtBr_4$; A. Gutbier and A. Rausch, **platinic bistripropylaminehydrobromide**, $2(C_3H_7)_3N.HBr.PtBr_4$; A. Ries, **platinic bistetrapropylammoniumbromide**, $2(C_3H_7)_4NBr.PtBr_4$; A. Ries, **platinic bismethyltripropylammoniumbromide**, $2(CH_3)(C_3H_7)_3NBr.PtBr_4$; A. Ries, **platinic bistriethylpropylammoniumbromide**, $2(C_2H_5)_3(C_3H_7)NBr.PtBr_4$; F. Bauriedel, and A. Gutbier and F. Bauriedel, **platinic bis-n-butylaminehydrobromide**, $2C_4H_9NH_2.HBr.PtBr_4$, and **platinic bis-iso-butylaminehydrobromide** ; A. Gutbier and A. Rausch, **platinic bisdi-iso-butylaminehydrobromide**, $2(C_4H_9)_2NH.HBr.PtBr_4$; A. Gutbier and A. Rausch, **platinic bistri-iso-butylaminehydrobromide**, $2(C_4H_9)_3N.HBr.PtBr_4$; A. Ries, and P. Groth, **platinic bisethyl-iso-butylaminehydrobromide**, $2(C_2H_5)(C_4H_9)NH.HBr.PtBr_4$; A. Ries, **platinic bistriethylbutylammoniumbromide**, $2(C_2H_5)_3(C_4H_9)NBr.PtBr_4$; A. Gutbier and A. Rausch, **platinic bis-iso-amylaminehydrobromide**, $2C_5H_{11}NH_2.HBr.PtBr_4$, **platinic bisdi-iso-amylaminehydrobromide**, $2(C_5H_{11})_2NH.HBr.PtBr_4$, and **platinic bistri-iso-amylaminehydrobromide**, $2(C_5H_{11})_3N.HBr.PtBr_4$; and A. Gutbier and A. Rausch, **platinic bisallylaminehydrobromide**, $2C_3H_5NH_2.HBr.PtBr_4$; **phenylammonium bromoplatinate**, $(C_6H_5.NH_3)_2PtBr_6$; **phenylmethylammonium bromoplatinate**, $\{(C_6H_5)(CH_3)NH_2\}_2PtBr_6$; **phenyldimethylammonium bromoplatinate**, $\{(C_6H_5)(CH_3)_2NH\}_2PtBr_6$; **phenylethylammonium bromoplatinate**, $\{(C_6H_5)(C_2H_5)NH_2\}_2PtBr_6$; **phenyldiethylammonium bromoplatinate**, $\{(C_6H_5)(C_2H_5)_2NH\}_2PtBr_6$; **bromophenylammonium bromoplatinate**, $(C_6H_4Br.NH_3)_2PtBr_6$, in its *o*-, *m*-, and *p*-forms ; **chlorophenylammonium bromoplatinate**, $(C_6H_4Cl.NH_3)_2PtBr_6$, in its *m*- and *p*-forms ; **2 : 4-dichlorophenylammonium bromoplatinate**, $(C_6H_3Cl_2.NH_3)_2PtBr_6$; **nitrosyldimethylammonium bromoplatinate**, $\{NO.NH(CH_3)_2\}_2PtBr_6$; **nitrosyldiethylammonium bromoplatinate**, $\{NO.NH(C_2H_5)_2\}_2PtBr_6$; **nitrosyldipropylbromoplatinate**, $\{NO.NH(C_3H_7)_2\}PtBr_6$; **nitrosyldi-iso-butyl-ammonium bromoplatinate**, $\{NO.NH(C_4H_9)_2\}_2PtBr_6$; **tolylammonium bromoplatinate**, $(CH_3.C_6H_4.NH_3)_2PtBr_6$, in its *o*-, *m*-, and *p*-forms; **tolyldimethylammonium bromoplatinate**, $\{C_6H_4(CH_3).NH(CH_3)_2\}_2PtBr_6$, in its *o*- and *p*-forms ; **2 : 4-tolylenediammonium bromoplatinate**, $(C_7H_{12}N_2)PtBr_6$; **3 : 4-tolylenediammonium bromoplatinate**, $(C_7H_{12}N_2)PtBr_6$; **methoxyphenylammonium bromoplatinate**, $(CH_3O.C_6H_4NH_3)_2PtBr_6$, in its *o*- and *p*-forms ; **ethyoxyphenylammonium bromoplatinate**, $(C_2H_5O.C_6H_4NH_3)_2PtBr_6$, in its *o*- and *p*-forms ; **tribenzylammonium bromoplatinate**, $\{(C_7H_7)_3NH\}_2PtBr_6$; **benzylmethylammonium bromoplatinate**, $\{(C_7H_7)(CH_3)NH_2\}_2PtBr_6$; **benzylidenemethylammonium bromoplatinate**, $\{CH(C_6H_5) : NH(CH_3)\}_2PtBr_6$; **xylylammonium bromoplatinate**, $\{(CH_3)_2C_6H_3.NH_3\}_2PtBr_6$, in its 1 : 2 : 3-, 1 : 3 : 4, and 1 : 4 : 5-forms ; **benzylammonium bromoplatinate**, $(C_7H_7.NH_3)_2PtBr_6$; **benzylethylammonium bromoplatinate**, $\{(C_7H_7)(C_2H_5)NH_2\}_2PtBr_6$; **benzylideneethylammonium bromoplatinate**, $\{CH(C_6H_5) : NH(C_2H_5)\}_2PtBr_6$; **benzylidenephenylammonium bromoplatinate**, $\{CHC_6H_5 : NH(C_6H_5)\}_2PtBr_6$; **benzidinium bromoplatinate**, $\{(C_6H_4)NH_3\}_2PtBr_6$; **phenylenediammonium bromoplatinate**, $\{C_6H_4(NH_3)_2\}PtBr_6$, in its *o*-, *m*-, and *p*-forms; **naphthylammonium bromoplatinate**, $(C_{10}H_7.NH_3)_2PtBr_6$, in its *α*- and *β*-forms ; **phenylbenzylammonium bromoplatinate**, $\{NH_2(C_6H_5)(C_7H_7)\}_2PtBr_6$; **phenylbenzylmethylammonium bromoplatinate**, $\{NH(CH_3)(C_6H_5)(C_7H_7)\}_2PtBr_6$; **2 : 4 : 5-trimethylphenylammonium bromoplatinate**, $\{(CH_3)_3(C_6H_2)N\}_2PtBr_6$.

A. B. Weinhagen prepared **choline bromoplatinate**, $(C_5H_{14}ON)_2PtBr_6$; **pyridinium**

bromoplatinate, $(C_5H_5N)_2H_2PtBr_5$; **betaine bromoplatinate,** $(C_5H_{12}O_2NCl)_2PtBr_5$; **arecaidine bromoplatinate,** $(C_7H_{11}O_2N)_2H_2PtBr_6.H_2O$; **arecoline dichlorotetrachloroplatinate,** $(C_8H_{13}O_2N)_2H_2PtCl_2Br_4$; and **nicoline bromoplatinate,** $(C_{10}H_{14}N_2)H_2PtBr_5.H_2O$; but not **morphine bromoplatinate,** or **hydrazine bromoplatinate.**

F. Bauriedel, C. J. Obermaier, and A. Gutbier and co-workers described **platinic bisanilinehydrobromide,** $2C_6H_5NH_2.HBr.PtBr_4$; F. Bauriedel, and A. Gutbier and co-workers, **platinic bistoluidinehydrobromide,** $2C_7H_7NH_2.HBr.PtBr_4$, with *o*-, *m*-, and *p*-tolyl; F. Bauriedel, and A. Gutbier and co-workers, **platinic bisxylidinehydrobromide,** $2C_8H_9NH_2.HBr.PtBr_4$, with the 1, 2, 4-, the 1, 3, 4-, and the 1, 4, 5-xylidine; C. J. Obermaier, and A. Gutbier and co-workers, **platinic bisnaphthylaminehydrobromide,** $2C_{10}H_7NH_2.HBr.PtBr_4$, with α- and β-naphthylamine; F. Bauriedel, and A. Gutbier and F. Bauriedel, **platinic ethylenediaminehydrobromide,** $C_2H_4(NH_2)_2.2HBr.PtBr_4$; and **platinic propylenediaminehydrobromide,** $C_3H_6(NH_2)_2.2HBr.PtBr_4$; F. M. Jäger studied the crystals of platinic trisethylenediaminochloride, Pt $en_3Br_4.1\frac{1}{2}H_2O$, and A. P. Smirnoff, **platinic trispropylenediaminobromide,** $[Pt(C_3H_6.N_2H_4)_3]Br_4$, in its racemic, dextro- and lævo-forms. S. G. Hedin prepared **platinic tetrabromobispyridine,** $[Pt(C_5H_5N)_2Br_4]$; F. Bauriedel, A. Gutbier and F. Bauriedel, and A. Gutbier and A. Rausch, **platinic bispyridinehydrobromide,** $2C_5H_5N.HBr.PtBr_4$, **3-methylpyridinium bromoplatinate,** $\{C_5H_5(CH_3)N\}_2PtBr_6$; **dimethylpyridinium bromoplatinate,** $\{C_5H_4(CH_3)_2N\}_2PtBr_6$; **trimethylpyridinium bromoplatinate,** $\{C_5H_3(CH_3)_3N\}_2PtBr_6$; **piperidinium bromoplatinate,** $(C_5H_{12}N)_2PtBr_6$; **iso-quinolinium bromoplatinate,** $(C_9H_8N)_2PtBr_6$, with α- and β-picoline; and **platinic bispicolinehydrobromide,** $2C_6H_7N.HBr.PtBr_4$; A. Gutbier and A. Rausch, **guanidine bromoplatinate,** $(C_2H_{18}N_6)PtBr_6$; **triphenylguanidine bromoplatinate,** $(NC_6H_5:C(NHC_6H_5)_2H_2PtBr_6$, the guanidine salt, $[Pt(CH_5N_3)Br_2]_2$, was prepared by M. Lesbre and E. Gardner; **platinic bislutidinehydrobromide,** $2C_7H_9N.HBr.PtBr_4$, **platinic biscollidinehydrobromide,** $2C_8H_{11}N.HBr.PtBr_4$, and **platinic bispiperidinehydrobromide,** $2C_5H_{11}N.HBr.PtBr_4$; A. Gutbier and A. Rausch, E. G. Cox and co-workers, F. Bauriedel, and A. Gutbier and F. Bauriedel, **platinic bisquinoline hydrochloride,** $2C_9H_7N.HBr.PtBr_4$, with ordinary and iso-quinoline; **α-picolinium bromoplatinate,** $\{(CH_3)C_5NH_5\}_2PtBr_6$; **quinolinium bromoplatinate,** $(C_9H_8N)_2PtBr_6$. L. Ramberg, **platinic tetrabromobisbenzonitrile,** $[Pt(C_6H_5.CN)_2Br_4]$; G. Wallin described **platinic tetrabromobisdiamidoacetate,** $[Pt(NH_2.CH_2.COOH)_2Br_4]$, and **platinic dibromobisglycine,** $[Pt(NH_2.CH_2.COO)_2Br_2]$; F. G. Mann, **platinic tetrabromotriaminopropanemonohydrochloride,** $[Pt(NH_2.CH_2.CHNH_2.CH_2NH_2)(HCl)Br_4]H_2O$. L. Tschugaeff, **platinic dibromobismethylethylglyoxime,** $Pt(NO.C.C_2H_5.CH_3.C.NOH)_2Br_2]$.

C. Enebuske and M. Weibull described **platinic tetrabromobismethylsulphine,** $[Pt\{(CH_3)_2S\}_2Br_4]$; C. W. Blomstrand, F. G. Angell and co-workers, and M. Weibull, **platinic tetrabromobisethylsulphine,** $[Pt\{(C_2H_5)_2S\}_2Br_4]$; C. Rudelius, H. Löndahl, and M. Weibull, **platinic tetrabromobispropylsulphine,** $[Pt\{(C_3H_7)_2S\}_2Br_4]$, represented by normal and isopropyl; F. G. Angell and co-workers, **platinic dichlorodibromobisethylsulphine,** $[Pt\{(C_2H_5)_2S\}_2Br_2Cl_2]$; P. C. Ray and N. N. Ghosh prepared complexes with ethylamine, $Pt_4Br_2.3(C_2H_5)_2S_2.(C_2H_5)NH_2$; with pyridine, $Pt_2Br_2,(C_2H_5)_2S_2.2C_5H_5N$; with benzylamine, $Pt_6Br_2.5(C_2H_5)_2S_2.2C_7H_7NH_2$; with phenylhydrazine, $Pt_{10}Br_2.9(C_2H_5)_2S_2.2C_6H_5.NH.NH_2$; with tripropylamine, $Pt_{10}Br_2.9(C_2H_5)_2S_2.N(C_3H_7)_3$; and with quinoline, $Pt_2Br_2(C_2H_5)_2S_2.2C_9H_7N$. J. Petren, **platinic tetrabromoethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2Br_4]$, and **platinic tetrabromoethylsulphineethylselenine,** $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}Br_4]$.

A. J. Balard obtained **hydrobromoplatinic acid,** $H_2PtBr_6.9H_2O$, by the action of a mixture of hydrobromic and nitric acids on platinum. W. Pullinger recommended dissolving platinum sponge in hydrobromic acid saturated with bromine in a sealed glass tube at 180°, and E. Biilmann and A. C. Anderson boiled the spongy platinum with the hydrobromic acid and bromine in a flask fitted with a reflux condenser, and heated on a water-bath. V. Meyer and H. Züblin used the process; L. von Müller did not obtain a good yield; H. Töpsöe evaporated the red liquid over calcium dioxide, and dried the crystals over sulphuric acid. W. Halberstadt washed the product with carbon disulphide on an asbestos filter. A. Gutbier and F. Bauriedel, L. von Müller, F. Bauriedel, and A. Gutbier and A. Rausch repeatedly evaporated hydrochloroplatinic acid with conc. hydrobromic acid on a water-bath, added hydrobromic acid and bromine three or four times, repeating the evaporation after each addition. The residue is dissolved in hydrobromic acid, and the deep carmine-red soln. evaporated over barium oxide.

The carmine-red crystals were said by H. Töpsöe to be monoclinic prisms. When the crystals are confined over calcium chloride, the faces gradually become dull owing to the loss of hydrogen bromide; and the crystals melt at 100° giving off water, bromine, and hydrogen bromide, and over 100° there is formed a mixture

of platinous bromide and hydrobromoplatinic acid. The crystals deliquesce in air. L. Pigeon gave for the heat of formation in soln. $(Pt, 2Br_2, 2HBr)=60\cdot70$ Cals.; or $(PtBr_4, 2HBr)=18\cdot27$ Cals.; and J. Thomsen gave $(Pt, 2Br_2, 2HBr)=57\cdot64$ Cals. also in aq. soln.; and $(Pt, O_2, 6HBr.Aq.)=80\cdot36$ Cals. H. I. Schlesinger and R. E. Palmateer studied the conditions for the reaction $PtBr_6''+6Cl'=PtCl_6''+6Br'$. H. Töpsöe, and W. Halberstadt found the crystals to be freely soluble in water, alcohol, ether, chloroform, and acetic acid. L. Pigeon said that a soln. of a mol. of the acid with 2 mols. of silver nitrate forms silver bromoplatinate which becomes colourless when the mixture is boiled for a long time. Hydrobromoplatinic acid furnishes a series of **bromoplatinates** isomorphous with the chloroplatinates. H. I. Schlesinger and R. E. Palmateer discussed the relative stabilities of the halogenoplatinates.

H. Töpsöe prepared **ammonium bromoplatinate,** $(NH_4)_2PtBr_6$, by adding ammonium bromide to an aq. soln. of hydrobromoplatinic acid, or, according to W. Halberstadt, to an aq. soln. of platinic bromide, and drying the product at 100°. The process was also employed by C. J. Obermaier, and A. Gutbier and co-workers. E. H. Archibald dissolved platinum electrolytically in hydrobromic acid, and added a dil. soln. of ammonium bromide with continuous stirring as in the case of the chloroplatinate. G. Méker observed that the metal is rapidly attacked by a fused mixture of ammonium sulphate and bromide under conditions where it is not attacked by either reagent alone. The red ammonium bromoplatinate which is formed is readily separated because it is insoluble in the ammonium salts. Ammonium bromoplatinate crystallizes from hot soln. in cubic crystals with the octahedral faces highly developed, but when deposited from cold soln., the cubic faces are the more prominent. The crystals are carmine-red, orange-red, or brownish-red. E. Carozzi found the crystals are isomorphous with the corresponding salts of tin, lead, and selenium. H. Töpsöe, and E. Carozzi gave 4·20 for the sp. gr., and E. H. Archibald, 4·265 at 24°/4°. The mol. vol. is 169·9. E. H. Archibald found that the crystals are decomposed at a temp. exceeding 185°; and P. C. Ray and A. C. Ghosh found that platinum, bromine, ammonium bromide, hydrogen bromide, and nitrogen are formed at higher temp. J. Thomsen gave for the heat of formation, $(Pt, 2Br_2, 2NH_4Br, Aq.)=57\cdot16$ Cals. W. Halberstadt found that the salt is sparingly soluble in water, 100 parts of soln. at 20° contain 0·59 part of the salt; and H. Töpsöe, that at 15°, 100 parts of water dissolve 0·5 part of salt. E. H. Archibald and J. W. Kern observed for the solubility, S grms. $(NH_4)_2PtBr_6$ per 100 grms. of water:

	0·2°	7·3°	19·0°	25·0°	50·0°	60°	80°	99°
S .	0·4165	0·5002	0·6438	0·7384	1·2087	1·5780	2·3002	3·5866

and for soln. with C mol NH_4Br per litre, at 20°:

C	2·000	1·000	0·200	0·100
S	0·0032	0·0080	0·0168	0·0359

P. A. von Bonsdorff, C. J. Obermaier, L. von Müller, W. Halberstadt, L. Pitkin, and A. Gutbier and co-workers prepared **potassium bromoplatinate,** K_2PtBr_6, by adding a soln. of potassium bromide to hydrobromoplatinic acid; E. Biilmann and A. C. Anderson washed the precipitate with ice-cold water, and then with alcohol. E. H. Archibald added a dil. soln. of potassium bromide slowly and with constant stirring to a soln. of platinum dissolved electrolytically in hydrobromic acid. G. Méker found that platinum is rapidly attacked by a fused mixture of ammonium sulphate and potassium bromide, and obtained crystals of potassium bromoplatinate as in the case of the corresponding ammonium salt. The yield is bad if a mixture of potassium sulphate and bromide is employed. The carmine-red, conc. soln. deposits octahedral crystals belonging to the cubic system, when evaporated spontaneously. M. Mathieu found that the X-radiogram corresponds with that of the analogous chloroplatinate, and that the space-lattice has $a=10\cdot35$

A., and there are 4 mols. per unit cell. H. Töpsöe gave 4·51 for the sp. gr.; C. H. D. Boedeker, 4·68; E. H. Archibald, 4·658 at 24°/4°; and R. Klement, 4·537 at 25°/4°, and 166·0 for the mol. vol. P. A. von Bonsdorff observed that the salt decrepitates when heated, at the same time it acquires a darker colour, and then decomposes with the evolution of bromine vapours. It is more stable than the corresponding chloroplatinate, and, added E. H. Archibald, it can be heated to 400° without decomposition. J. Thomsen gave for the heat of formation (Pt, $2Br_2$, 2KBr)=59·26 Cals., (Pt, $2Br_2$, 2KBr, Aq.)=57·16 Cals.; and ($K_2PtBr_{4soln.}$, Br_{2gas}) =25·35 Cals., and for heat of solution, −12·26 Cals. H. I. Schlesinger and M. W. Tapley studied the absorption spectrum. A. Miolati gave for the electrical conductivity, λ, of soln. with a gram-equivalent of the salt in v litres:

v	64	128	256	512	1024
λ	113·1	120·4	126·5	134·4	143·3

and for a dil. soln. with v=128, the conductivity increases with time owing to hydrolysis, thus:

Time . . .	0	1	2	5	30	30	90 min.
λ	105·7	110·4	112·6	113·6	118·4	119·7	120·3

N. Demassieux and J. Heyrovsky studied the dissociation of the salt in soln.; and H. I. Schlesinger and R. E. Palmateer, the relative stability of the halogen salts. The salt is sparingly soluble in water, and W. Halberstadt observed that 100 parts of a sat., aq. soln., at 20°, contain 2·02 parts of the dry salt. P. A. von Bonsdorff observed that the salt is insoluble in water. E. H. Archibald and W. A. Gale's observations on the hydrolysis of the salt in aq. soln., measured with that of the corresponding chloroplatinate, are summarized in Fig. 90. According to M. Vèzes, an excess of potassium nitrite converts a boiling soln. of potassium bromoplatinate into potassium nitritoplatinite; and with 4 mols. of potassium nitrite there is formed potassium dinitritodibromoplatinite.

C. J. Obermaier, A. Gutbier and co-workers, and L. von Müller prepared **rubidium bromoplatinate,** Rb_2PtBr_6, in yellowish-red octahedra, by adding a soln. of rubidium bromide to hydrobromoplatinic acid, and recrystallizing the precipitate from a soln. in hydrobromic acid. They also prepared **cæsium bromoplatinate,** $CsPtBr_6$, in reddish-yellow octahedra, by mixing soln. of cæsium bromide and hydrobromoplatinic acid, and recrystallizing the precipitate from a soln. in hydrobromic acid.

P. A. von Bonsdorff prepared **sodium bromoplatinate,** $Na_2PtBr_6.6H_2O$, by mixing aq. soln. of sodium bromide and hydrobromoplatinic acid; and J. Thomsen, by boiling mixed soln. of platinic chloride and hydrobromic acid, adding the equivalent of 2 mols. of sodium bromide, evaporating to dryness, and recrystallizing from aq. soln. The dark red crystals of the *hexahydrate* were found by H. Töpsöe to be triclinic pinacoids with the axial ratios $a : b : c$=0·9806 : 1 : 0·8553, and α=101° 9½′, β=126° 53½′, and γ=73° 50½′; and they are isomorphous with the corresponding chloride. The sp. gr. is 3·323, and the mol. vol. 250·2. P. A. von Bonsdorff observed that the crystals are stable in air, and H. Töpsöe, that in moist air the faces of the crystals become matte. W. Peters found that the crystals lose all their water at 150°, and becomes reddish-violet. J. Thomsen gave for the heat of formation of the hexahydrate from the anhydrous salt 18·54 Cals., and (Pt, $2Br_2$, 2NaBr) =46·79 Cals.; (Pt, $2Br_2$, 2NaBr, $6H_2O$)=65·33 Cals.; (Pt, $2Br_2$, 2NaBr, Aq.) =57·16 Cals.; the heat of soln. of the anhydrous salt is 99·9 Cals., and of the hexahydrate, −8·55 Cals. P. A. von Bonsdorff said that the hexahydrate is soluble in water and alcohol; and J. Thomsen, that the anhydrous salt attracts moisture from the air. W. Peters found that the anhydrous salt slowly absorbs dry ammonia to form **sodium hexamminobromoplatinate,** $Na_2PtBr_6.6NH_3$, which, in vacuo, forms **sodium pentamminobromoplatinate,** $Na_2PtBr_6.5NH_3$. H. I. Schlesinger and R. E. Palmateer studied the photochemical reaction, $Na_2PtBr_6+6NaCl \rightleftharpoons Na_2PtCl_6+6NaBr$.

H. Töpsöe prepared **copper bromoplatinate,** $CuPtBr_6.8H_2O$, by spontaneously evaporating mixed soln. of cupric bromide and hydrobromoplatinic acid. The brown plates are probably rhombic with the axial ratios $a : b : c = 0{\cdot}744 : 1 : 1{\cdot}009$. The crystals of the *octohydrate* deliquesce in air, and at 100° form a brown powder of the anhydrous salt. L. Pigeon, and A. Miolati and I. Bellucci obtained **silver bromoplatinate,** Ag_2PtBr_6, from soln. of silver nitrate and hydrobromoplatinic acid. L. Pigeon gave for the heat of formation $(PtBr_4, 2AgBr) = 10{\cdot}37$ Cals. A. Miolati and I. Bellucci found that the salt is not decomposed in a sealed tube at 150°, and it is stable when boiled with a large excess of water.

P. A. von Bonsdorff, and H. Töpsöe prepared **calcium bromoplatinate,** $CaPtBr_6.12H_2O$, by neutralizing hydrobromoplatinic acid with calcium carbonate, and evaporating the soln. over sulphuric acid. The scarlet-red crystals are monoclinic; they are stable in air and soluble in water. H. Töpsöe prepared **strontium bromoplatinate,** $SrPtBr_6.10H_2O$, in a similar manner; the tabular crystals have a sp. gr. of 2·923, and mol. vol. 323·2. They are a little deliquescent. H. Töpsöe, and P. A. von Bonsdorff prepared **barium bromoplatinate,** $BaPtBr_6.10H_2O$. The reddish-brown crystals are probably monoclinic; the sp. gr. is 3·713, and the mol. vol., 267·8. The crystals are stable in dry air, but deliquesce in moist air. They are dehydrated at 120°.

H. Töpsöe, and P. A. von Bonsdorff prepared **magnesium bromoplatinate,** $MgPtBr_6.12H_2O$, by cooling a hot soln., or by spontaneously evaporating a soln. of magnesium bromide and hydrobromoplatinic acid. The dark scarlet-red crystals are, according to H. Töpsöe, and H. Töpsöe and C. Christiansen, trigonal with the axial ratio $a : c = 1 : 0{\cdot}6974$, and $\alpha = 106°\ 54'$; the optical character is negative; the sp. gr. is 2·802, and the mol. vol. 327·4. The crystals are fairly stable in air; but over calcium chloride they lose 6 mols. of water, forming an orange-red powder. The weight remains constant up to 120°. The remainder of the water is lost with decomposition at 180°. P. A. von Bonsdorff, and H. Töpsöe obtained **zinc bromoplatinate,** $ZnPtBr_6.12H_2O$, as in the case of the magnesium salt. The carmine red, deliquescent crystals were found by H. Töpsöe, and H. Töpsöe and H. Christiansen to be trigonal with the axial ratio $a : c = 1 : 0{\cdot}6990$, and $\alpha = 106°\ 52'$; the optical character is negative; the sp. gr. 2·877, and the mol. vol. 333·4.

C. J. Obermaier prepared **thallous bromoplatinate,** Tl_2PtBr_6, from a soln. of thallous bromide and hydrobromoplatinic acid. The salt is yellowish-red, and it is almost insoluble in water and in aq. hydrobromic acid. H. Töpsöe obtained **lead bromoplatinate,** $PbPtBr_6$, by evaporating a soln. of lead bromide and hydrobromoplatinic acid. The gum-like mass furnishes a yellowish-brown powder of sp. gr. 6·025, and mol. vol. 146·8. The salt suffers no change at 120°. It is readily soluble in water.

S. M. Jörgensen obtained **chromic hexamminobromoplatinate,** $[Cr(NH_3)_6]_2(PtBr_6)_3.4H_2O$, as a scarlet precipitate, by mixing soln. of chromic hexamminobromide and sodium bromoplatinate. The quadratic, and eight-sided plates lose all their water when confined over sulphuric acid. He also obtained **chromic bromopentamminobromoplatinate,** $[Cr(NH_3)_5Br]PtBr_6$, by mixing soln. of the corresponding bromide, and sodium bromoplatinate. The dark orange-red crystalline precipitate is sparingly soluble in water, and is decomposed by hydrobromic acid (1 : 1). C. Christiansen prepared **chromic aquopentamminobromoplatinate,** $[Cr(NH_3)_5(H_2O)]Br(PtBr_6)$, by the action of the corresponding bromide on sodium bromoplatinate. The dark red, six-sided, pyramidal crystals form chromic bromopentammine bromide when treated with hydrobromic acid.

H. Töpsöe prepared **manganese bromoplatinate,** $MnPtBr_6.12H_2O$, by slow cooling, or the spontaneous evaporation of the soln. obtained by saturating hydrobromoplatinic acid with manganese carbonate. The red crystals of the *dodecahydrate* are isomorphous with those of the magnesium salt, and they are trigonal with the axial ratio $a : c = 1 : 0{\cdot}7025$, and $\alpha = 106°\ 45'$; the sp. gr. is 2·759, and the mol. vol. 343·7. E. Herlinger gave 342·7 for the mol. vol. The crystals are fairly

stable in air, they effloresce over calcium chloride ; lose 10½ mols. of water at 110° to 120°, and any further loss of water is attended by the decomposition of the salt. P. A. von Bonsdorff obtained the *hexahydrate* in dark red, six-sided prisms isomorphous with hexahydrated magnesium chloroplatinate. The crystals are stable in dry air ; deliquescent in moist air.

H. Töpsöe obtained **cobalt bromoplatinate,** $CoPtBr_6.12H_2O$, by evaporating over sulphuric acid the soln. obtained by saturating hydrobromoplatinic acid with cobalt carbonate. The carmine-red, deliquescent crystals are trigonal with the axial ratio $a : c=1 : 0·6979$, and $\alpha=106° 53'$. H. Töpsöe and C. Christiansen said that the optical character is positive ; and H. Töpsöe, that the sp. gr. is 2·762, and the mol. vol. 344·6. E. Herlinger gave 343·9 for the mol. vol. S. M. Jörgensen obtained **cobaltic hexamminobromoplatinate,** $[Co(NH_3)_6]Br(PtBr_6).H_2O$, by the action of the corresponding bromide on sodium bromoplatinate. The crimson-red crystals lose half a mol. of water at 100°. S. M. Jörgensen prepared **cobaltic aquopentamminobromoplatinate,** $[Co(NH_3)_5(H_2O)]_2(PtBr_6)_3.4H_2O$, by the action of sodium bromoplatinate on the chloride of the series. The cinnabar-red, quadratic or six-sided plates of the *tetrahydrate* are orange-yellow in transmitted light, and they lose 4 mols. of water at 100° ; he also obtained the *monohydrate* of $[Co(NH_3)_5(H_2O)]Br(PtBr_6)$, in dark red, six-sided prisms or pyramids, which do not lose water over sulphuric acid, but at 100°, 2 mols. of water are given off to form **cobaltic bromopentamminobromoplatinate,** $[Co(NH_3)_5Br]PtBr_6$. S. M. Jörgensen obtained this salt by the action of sodium bromoplatinate on the nitrate of the series. The reddish-brown crystals are soluble in water. He also obtained **cobaltic dibromobisethylenediaminebromoplatinate,** $[Co\,en_2Br_2]_2PtBr_6$, by the action of sodium bromoplatinate on the bromide of the series.

H. Töpsöe, and H. Töpsöe and C. Christiansen prepared **nickel bromoplatinate,** $NiPtBr_6.6H_2O$, by spontaneously evaporating the soln. obtained by saturating hydrobromoplatinic acid with nickel carbonate. The greenish-brown, deliquescent crystals are trigonal prisms with the axial ratio $a : c=1 : 0·5136$, and $\alpha=112° 16'$. The optical character is positive ; W. Biltz gave for the sp. gr. 3·715 ; and the mol. vol., 327·2. The crystals lose their water in a desiccator to form a yellow powder.

P. T. Cleve prepared **platinic hydroxybromotetramminobromide,** $[Pt(NH_3)_4(OH)Br]Br_2$, in yellow prisms, sparingly soluble in water, by the action of ammonium bromide on a hot soln. of the nitrate of the series. O. Calgren and P. T. Cleve prepared **platinic dihydroxytetramminobromide,** $[Pt(NH_3)_4(OH)_2]Br_2$, by the action of barium bromide on the corresponding sulphate. The evaporation of the filtered soln. furnishes colourless prisms, sparingly soluble in water. A mol of the salt in v litres of water at 20° was found by A. Werner to have the conductivity, μ :

v . .	125	250	500	1000
μ . .	204·7	217·4	226·5	235·5

A. Miolati and I. Bellucci stated that an aq. soln. of platinic bromide contains **dihydroxytetrabromoplatinic acid,** $H_2Pt(OH)_2Br_4$, and he inferred that a dibasic acid is present in this soln. from the electrometric titration of the soln. with aq. ammonia or sodium hydroxide, and from the electric conductivity, μ, of soln. with a mol of platinic bromide in v litres :

v . .	128	256	512	1024
μ . .	344·4	348·9	353·6	359·4

A. Miolati and I. Bellucci obtained lithium dihydroxytetrabromoplatinate, $Li_2Pt(OH)_2Br_4$, from a mixture of platinic bromide and lithium carbonate in warm water, and when the evolution of carbon dioxide ceased evaporating the liquid over sulphuric acid, in vacuo. The dark red, deliquescent mass obtained by adding alcohol to the syrup is very soluble in water. The liquid, obtained by adding 2 eq.

of sodium hydroxide in 0·1*N*-NaOH, has the mol. conductivity, μ, for soln. with a mol of **sodium dihydroxytetrabromoplatinate,** $Na_2Pt(OH)_2Br_4$, in v litres, at 25° :

v	32	64	128	256	512	1024
μ	105·3	109·2	114·9	118·5	122·9	125·6

where $\mu_{1024}-\mu_{32}=20·3$ in accord with the value for the neutral salt of a dibasic acid. Dark brown **silver dihydroxytetrabromoplatinate,** $Ag_2Pt(OH)_2Br_4$, is obtained by adding a small excess of silver nitrate to a soln. of platinic bromide, washing the precipitate with cold water, and drying it at 100°. Neither by the action of barium hydroxide nor carbonate on an aq. soln. of platinic bromide was it possible to prepare **barium dihydroxytetrabromoplatinate,** $BaPt(OH)_2Br_4$. A dark red precipitate of **mercuric dihydroxytetrabromoplatinate,** $HgPt(OH)_2Br_4$, is produced when mercuric acetate is added to an aq. soln. of platinic bromide. The silver, mercury, and thallous salts were also discussed by F. Reiff. The brown precipitate of **thallous dihydroxytetrabromoplatinate,** $Tl_2Pt(OH)_2Br_4$, is formed when thallous acetate is added to an aq. soln. of platinic bromide with lead acetate, dark brown **lead dihydroxytetrabromoplatinate,** $PbPt(OH)_2Br_4$, is precipitated. S. M. Jörgensen obtained **chromic hydroxydecamminobromoplatinate,** $[Cr_2(OH)(NH_3)_{10}]_2Br_4(PtBr_6)3·4H_2O$, in salmon-red, four-sided crystals, by the action of hydrobromoplatinic acid on the thiocyanatobromide. L. A. Tschugaeff prepared **platinic bromopentamminobromide,** $[Pt(NH_3)_5Br]Br_3$, in yellow prisms ; and **platinic chloropentamminobromide,** $[Pt(NH_3)_5Cl]Br_3$, in pale yellow, sparingly soluble needles.

P. T. Cleve obtained **platinic dibromohexammino-μ-diaminochloride,** $[Br(NH_3)_3Pt(NH_2)_2Pt(NH_3)_3Br]Cl_4$, by the action of an excess of hydrochloric acid on the corresponding nitrate. The yellowish-white crystals can be dried over sulphuric acid or in vacuo. P. T. Cleve prepared **platinic dichlorotetramminobromide,** $[Pt(NH_3)_4Cl_2]Br_2$, by the action of ammonium bromide on the corresponding nitrate ; and M. Raewsky, by the action of bromine on a boiling soln. of platinous tetramminobromide. The orange-yellow, crystalline powder is sparingly soluble in water ; fuming hydrochloric acid converts it into $[Pt(NH_3)_4ClBr]Cl_2$; and silver nitrate precipitates silver chloride and bromide from the hot soln. Likewise **platinic dibromotetramminochloride,** $[Pt(NH_3)_4Br_2]Cl_2$, was produced by the action of ammonium chloride on the corresponding nitrate. The salts were studied by H. D. K. Drew and co-workers. P. T. Cleve obtained **platinic chlorobromotetramminochloride,** $[Pt(NH_3)_4ClBr]Cl_2$, by the action of an excess of fuming hydrochloric acid on the dichlorotetramminochromide, on the dibromotetramminochloride, or on the hydroxybromotetramminonitrate, and drying the yellow powder over sulphuric acid, or at 100°. L. A. Tschugaeff prepared yellow crystalline **platinic amidobromotetramminobromide,** $[Pt(NH_3)_4(NH_2)Br]Br_2$; and **platinic amidochlorotetramminobromide,** $[Pt(NH_3)_4(NH_2)Cl]Br_2$.

A. Werner described **platinic dibromobispropylenediaminochloride,** $[Pt\{(C_3H_5)(NH_2)_2\}_2Br_2]Cl_2$; **platinic dibromopropylenediaminediamminochloride,** $[Pt(NH_3)_2\{C_3H_3(NH_2)_2\}Br_2]Cl_2$; S. G. Hedin, **platinic dichlorodibromobispyridine,** $[Pt(C_5H_5N)_2Cl_2Br_2]$; C. Enebuske, **platinic dichlorodibromobismethylsulphine,** $[Pt\{(CH_3)_2S\}_2Cl_2Br_2]$; C. W. Blomstrand, and M. Weibull, **platinic dichlorodibromobisethylsulphine,** $[Pt\{(C_2H_5)_2S\}_2Cl_2Br_2]$; C. Rudelius, **platinic dichlorodibromobispropylsulphine,** $[Pt\{(C_3H_7)_2S\}_2Cl_2Br_2]$; H. Löndahl, and M. Weibull, **platinic dichlorodibromobisbutylsulphine,** $[Pt\{(C_4H_9)_2S\}_2Cl_2Br_2]$, with iso- and secondary butyl ; J. Petren, **platinic dichlorodibromobisethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2Cl_2Br_2]$, **platinic chlorotribromobisethylselenine,** $Pt\{(C_2H_5)_2Se\}_2ClBr_3]$, and **platinic dichlorodibromoethylsuphinethylselenine,** $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}Cl_2Br_2]$; and A. Cahours and H. Gal, **platinic dichlorodibromobisethylphosphine,** $[Pt\{P(C_2H_5)_3\}_2Cl_2Br_2]$; and A. Rosenheim and W. Levy, **platinic tetrabromobismethylphosphate,** $[Pt\{OP(OCH_3)_3\}_2Br_4]$; **platinic tetrabromobisethylphosphate,** $PtBr_4\{PO(OC_2H_5)_3\}_2$; and **platinic dibromodichloroethylphosphate,** $PtCl_2Br_2.PO(OC_2H_5)_3$.

G. Gore reported a complex **silver fluobromoplatinate,** nAgBr.PtF_4, is formed when silver fluoride in an atm. of bromine is melted in a platinum crucible. L. Pitkin reported a series of **potassium chlorobromoplatinates,** $K_2PtCl_nBr_{6-n}$, to be

formed by crystallization from soln. with different proportions of the chloro- and bromoplatinates. L. Pitkin said that the products are not mixtures because a particular compound can be obtained by different modes of preparation, and solubility determinations give constant values. On the other hand, C. H. Herty found that the products change in composition with small changes in the ratio of the two salts in soln., and he accordingly inferred that the products are isomorphous mixtures or solid soln. R. Klement also obtained **potassium tetrachlorodibromoplatinate,** $K_2PtCl_4Br_2$, by the action of bromine on the chloroplatinate; he gave 3·826 for the sp. gr. at 25°/4° and 150·3 for the mol. vol. L. Pitkin reported **potassium pentachlorobromoplatinate,** K_2PtCl_5Br, to be obtained by crystallization from a warm soln. of 5 mols. of the chloroplatinate, and 1 mol. of the bromoplatinate; and **potassium tetrachlorodibromoplatinate,** $K_2PtCl_4Br_2$, from a soln. of 4 grms. of potassium bromide in the smallest possible quantity of water, up to 2 c.c. of conc. hydrochloric acid, and 0·5 grm. of platinic chloride. A. Miolati said that this product is also obtained by treating potassium chloroplatinite with bromine. The salt can be recrystallized from warm water; it furnishes orange-red, dichroic, cubic crystals. The electrical conductivity, λ, of a cold aq. soln. changes with time so that for half a mol of $K_2PtCl_4Br_2$ in 128 litres, the change with time, in minutes, is:

Time . . .	0	1	5	10	15	125	215	255
λ . . .	116·4	117·8	118·9	120·3	128·8	137·4	147·1	149·5

and the maximum value was attained in 22 hrs., and the results for a half mol of the salt in v litres are represented by λ_1, whilst the values with a soln. of two-thirds an eq. of potassium chloroplatinate are represented by λ_2.

v . .	64	128	256	512	1024
λ_1 . .	145·1	157·1	167·0	175·6	188·8
λ_2 . .	139·0	144·9	153·0	162·1	173·3

A. Miolati and I. Bellucci prepared **silver tetranitritodibromoplatinate,** $Ag_2Pt(NO_2)_4Br_2$. L. Pitkin also obtained **potassium trichlorotribromoplatinate,** $K_2PtCl_3Br_3$, from a soln. of 488 parts of the chloroplatinate and 755 parts of the bromoplatinate; L. Pigeon, and L. Pitkin obtained **potassium dichlorotetrabromoplatinate,** $K_2PtCl_2Br_4$, from a soln. of 1·4658 grms. of the chloroplatinate, and 4·5336 grms. of the bromoplatinate. L. Pitkin also reported **potassium chloropentabromoplatinate,** $K_2PtClBr_5$, in ruby-red, octahedral crystals.

S. M. Jörgensen described **cobaltic chloropentamminobromoplatinate,** $[Co(NH_3)_5Cl]PtBr_6$, in yellowish-brown, rectangular plates, obtained by the action of potassium bromoplatinate on the nitrate of the series; **cobaltic bromopentamminochloroplatinate,** $[Co(NH_3)_5Br]PtCl_6$, as a reddish-brown, crystalline precipitate, soluble in water, by the action of hydrochloroplatinic acid on the chloride of the series. A. Werner and A. Wolberg obtained **cobaltic dibromotetramminochloroplatinate,** $[Co(NH_3)_4Br_2]PtCl_6$, by the action of hydrochloroplatinic acid on the chloride or sulphate of the series. The yellowish-green scales are freely soluble in water. S. M. Jörgensen prepared **cobaltic dibromobisethylenediaminechloroplatinate,** $[Co\,en_2Br_2]_2(PtCl_6).3H_2O$, in pale green needles, obtained by the action of hydrochloroplatinic acid on the bromide of the series. It loses 3 mols. of water over sulphuric acid, or at 100°.

P. T. Cleve prepared **platinic hydroxychlorotetramminobromide,** $[Pt(NH_3)_4(OH)Cl]Br_2$, in pale yellow prisms, by the action of ammonium bromide on a soln. of the nitrate, and drying the product at 100°; and likewise **platinic hydroxybromotetramminochloride,** $[Pt(NH_3)_4(OH)Br]Cl_2$, in straw-yellow, four-sided, rhombic prisms, by the action of ammonium chloride on a soln. of the nitrate, and drying the product over sulphuric acid. P. T. Cleve obtained **platinic bromochlorotetramminochloride,** $[Pt(NH_3)_4BrCl]Cl_2$, by the action of hydrochloric acid on the bromosulphatotetramminosulphate. G. Wallin prepared **platinic**

dichlorodibromobisamidoacetate, $[Pt(NH_2.CH_2.COOH)_2Cl_2Br_2]$; and **platinic dichlorodibromobisethylamidoacetate,** $[Pt(NH_2.CH_2.COOC_2H_5)_2Cl_2Br_2]$. E. Pomey, **platinic dichlorodibromobisethylphosphite,** $[Pt\{P(OC_2H_5)_3\}_2Cl_2Br_2]$; P. Klason, **platinic chlorodibromoethylmercaptidoethylsulphine,** $[Pt\{(C_2H_5)_2S\}(C_2H_5S)ClBr_2]$; J. Petren, **platinic dichlorodibromoethylsulphinoethylselenine,** $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}Cl_2Br_2]$; E. Pomey, **platinic dichlorodibromoethylphosphite,** $[Pt\{P(OC_2H_5)_3\}Cl_2Br_2]$; A. Rosenheim and W. Loewenstamm, **platinic dichlorodibromomethylphosphate,** $[Pt\{OP(OCH_3)_3\}Cl_2Br_2]$, and **platinic dichlorodibromoethylphosphate,** $[Pt\{OP(OC_2H_5)_3\}Cl_2Br_2]$.

P. T. Cleve prepared **platinic trans-dibromodinitritodiammine,** $[Pt(NH_3)_2(NO_2)_2Br_2]$ and **platinic cis-dibromodinitritodiammine**; and J. Petren, **platinic dibromodinitritoethylsulphineethylselenine,** $[Pt\{(C_2H_5)_2S\}\{C_2H_5)_2Se\}(NO_2)_2Br_2]$.

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§ 25. Platinous Iodide

G. van Praagh and E. K. Rideal [1] assumed that platinum subiodide, or platinum monoiodide, PtI, is formed when iodine attacks platinum at a high temp.—*vide supra*, the action of iodine on platinum. J. L. Lassaigne prepared **platinous iodide**, or **platinum diiodide**, PtI_2, by warming platinous chloride with an aq. soln. of potassium iodide for 15 minutes, and drying the washed product. G. Clementi found it difficult to prepare this salt. H. Töpsöe added that if the digestion is too short, the metathesis is incomplete, and if too long, some platinous iodide is converted into platinum and platinic iodide. W. Peters recommended treating platinous iodide with hydriodic acid of sp. gr. 1·96, and drying the product at 100°; and L. Ramberg, dissolving a mol. of potassium chloroplatinite in about 5 times its weight of boiling water, and adding 2 mols. of potassium iodide in a (1 : 4)-soln., warming the mixture twice on a water-bath for a short time, allowing the soln. to stand over night, washing the product with water, and drying at 90°.

The soft black powder, said J. L. Lassaigne, sticks to the fingers like lampblack; it is tasteless, odourless, and stable in air. R. Klement gave 6·403 for the sp. gr. at 25°/4°, and 70·1 for the mol. vol. When heated to the b.p. of mercury, it gives off iodine, and leaves spongy platinum behind. Water, and cold hydrochloric acid have no action on the salt; cold, aq. hydriodic acid, of sp. gr. 1·038, acts on it forming platinum and platinic iodide which passes into soln.; a hot, aq. soln. of potassium iodide acts similarly, but the greater part of the platinous iodide remains undecomposed. Conc. sulphuric and nitric acids have no action on the salt. When digested with aq. ammonia, a dark yellowish-green powder is formed, which, when heated, gives off water, ammonium iodide, and ammonia. W. Peters said that the salt absorbs dry ammonia—*vide infra*. J. L. Lassaigne found that alcohol has no action on platinous iodide, when the salt is digested with potash lye or soda lye, part of the platinous oxide which is formed separates as a black powder, and part passes into soln.

W. Peters obtained orange-red **platinous hexamminoiodide**, $PtI_2.6NH_3$, by

the action of dry ammonia on platinous iodide; and this compound, in vacuo, furnishes **platinous tetramminoiodide,** $[Pt(NH_3)_4]I_2$. L. Ramberg prepared the tetramminoiodide by heating a mol of platinous iodide with dil. aq. ammonia (1000 c.c. water and 500 c.c. ammonia of sp. gr. 0·91); and J. Reiset, by the action of a soln. of barium iodide on a boiling soln. of the tetramminosulphate, and also by the action of ammonia on trans-diiodo-diammine. The dry salt does not change at 120°. The tabular crystals change their colour when exposed to air. When the aq. soln. is boiled, it forms the diiododiammine. A. A. Grinberg and B. V. Ptitsin studied the thermal decomposition of the salt. The salt forms with mercuric iodide **platinous tetramminoiodomercurate,** $[Pt(NH_3)_4]HgI_3)_2$. L. A. Tschugaeff and M. S. Grigorieff prepared **platinous dihydrazinodiamminoiodide,** $[Pt(NH_3)_2(N_2H_4)_2]I_2$. A. Schleicher and co-workers prepared the *cis*- and *trans*-forms of **platinous bispyridinodiamminoiodide,** $[Pt(NH_3)_2py_2]I_2$; and **platinous bisethylenediaminoiodide,** $[Pt\,en_2]I_2$, in its cis- and trans-forms; and studied its passage to $[Pt_2\,en_4I(H_2O)_{12}]I{\cdot}5H_2O$ by the action of acids.

P. T. Cleve, and A. Schleicher and co-workers prepared **platinous cis-diiododiammine,** $[Pt(NH_3)_2I_2]$, by mixing conc. soln. of potassium iodide and the cis-nitrate, and drying the product at 100°. The yellow crystals are sparingly soluble in boiling water; iodine forms a polyiodide; hot aqua regia forms the tetrachlorodiammine; and ammonia, the diiodotetrammine. J. Reiset, and A. Schleicher and co-workers prepared **platinous trans-diiododiammine** by boiling an aq. soln. of the tetramminoiodide; and L. Ramberg, by passing steam through a soln. of the tetramminoiodide. L. A. Tschugaeff prepared the diiododiammine by boiling a soln. of platinous iodide with aq. ammonia; and F. G. Mann, platinous iododiaminodiethylaminoiodide, $[IPt(H_2N.C_2H_4)_2NH]I$. The orange-yellow crystalline powder is soluble in aq. ammonia forming, according to J. Reiset, the tetramminoiodide. According to P. T. Cleve, the trans-salt reacts with iodine to form tetraiododiammine; and with hot aqua regia, to form trans-tetrachlorodiammine. E. Koefoed prepared a chocolate-brown variety.

S. M. Jorgensen described **platinous diiodobismethylamine,** $[Pt(CH_3NH_2)_2I_2]$. L. A. Tschugaeff prepared this salt by boiling a soln. of platinous iodide with methylamine; and F. G. Mann, **platinous bis-β-methyltrimethylenediaminoiodide,** $[Pt\{CH(CH_3)(CH_2.NH_2)_2\}_2]I_2$; and **platinous bis-αβγ-triaminopropanobromide,** $[Pt\{NH_2.CH_2.CH.NH_2.CH_2.NH_2\}_2]I_2$. H. Reihlen discussed **platinous diiodo-ββ′β″-triaminotriethylamine,** $[PtN(C_2H_4.NH_2)_3.I_2]$, prepared by F. G. Mann. F. Mylius and F. Forster described **trimethylaminocarbonyltriiodoplatinite,** $[Pt(CO)I_3]H\{(CH_3)_3N\}$, or $(CH_3)_3N.HI.PtI_2.CO$; P. T. Cleve, **platinous bisdimethylaminediamminoiodide,** $[Pt(NH_3)_2(C_2H_5NH_2)_2]I_2$; P. T. Cleve, **platinous diiodoethylamineammine,** $[Pt(NH_3)(C_2H_5NH_2)I_2]$, and **platinous diiodoanilineammine.** $[Pt(NH_3)(C_6H_5NH_2)I_2]$; and A. Schleicher and co-workers, cis- and trans-forms of **platinous diiodobisaniline,** $[Pt(C_6H_5NH_2)_2I_2]$; S. M. Jörgensen, **platinous diiodobispropylamine,** $[Pt(C_3H_7NH_2)_2I_2]$; A. Werner, **platinous bispropylenediamineiodide,** $[Pt\{C_3H_6(NH_2)_2\}_2]I_2$; S. G. Hedin, **platinous diiodobispyridine,** $[Pt(C_5H_5N)_2I_2]$, and **platinous quaterpyridineiodide,** $[Pt(C_5H_5N)_4]I_2$; F. Mylius and F. Förster, **platinous diiodocarbonyl,** $[Pt(CO)I_2]$; L. A. Tschugaeff and co-workers, **platinous dihydrazinoctomethylcarbylaminoiodide,** $[(CH_3.NC)_4Pt(N_2H_3)_2Pt(CH_3NC)_4]I_2.4H_2O$; and **platinous dihydrazinoctoethylcarbylaminoiodide,** $[(C_2H_5.NC)_4Pt(N_2H_3)_2Pt(C_2H_5.NC)_4]I_2$.

M. Weibull, and C. Enebuske described **platinous diiodobismethylsulphine,** $[Pt\{(CH_3)_2S\}_2I_2]$; M. Weibull, A. Hamberg, K. A. Hofmann and W. O. Rabe, P. Klason, and C. W. Blomstrand, **platinous diiodobisethylsulphine,** $[Pt\{(C_2H_5)_2S\}_2I_2]$; C. Rudelius, and M. Weibull, **platinous diiodobispropylsulphine,** $[Pt\{(C_3H_7)_2S\}I_2]$, with normal and iso-propyl, and **platinous diiodobispropylsulphineiodoplatinite,** $[Pt\{(C_3H_7)_2S\}_2I_2]PtI_2$; K. A. Hofmann and W. O. Rabe, **platinous diiodobismethylethylsulphine,** $[Pt\{(CH_3)(C_2H_5)S\}_2I_2]$; H. Löndahl, and P. Klason, **platinous diiodoethylsulphineammine,** $[Pt(NH_3)\{(C_2H_5)_2S\}I_2]$, in its cis- and trans-forms; M. Weibull, and C. Rudelius, **platinous diiodoethylsulphinepropylsulphine,** $[Pt\{(C_2H_5)_2S\}\{(C_3H_7)_2S\}I_2]$, with normal and iso-propyl; H. Löndahl, **platinous diiodobisbutylsulphine,** $[Pt\{(C_4H_9)_2S\}_2I_2]$, with normal, iso-, and secondary butyl, and **platinous diiodoethylsulphinebutylsulphine,** $[Pt\{(C_2H_5)_2S\}\{(C_4H_9)_2S\}I_2]$; C. W. Blomstrand and C. Rudelius, **platinous diiodobis-i-amylsulphine,** $[Pt\{(C_5H_{11})_2S\}_2I_2]$; H. Löndahl, **platinous diiodobisbenzylsulphine,** $Pt(C_6H_5CH_2)_2I_2]$, **platinous diiodoethylenesulphine,** $[Pt\{(C_2H_4)_2S_2\}I_2]$, and **platinous iodoethylenesulphineamminoiodide,** $[Pt(NH_3)\{(C_2H_4)_2S_2\}I]I$; S. Tyden, **platinous diiodobisthioglycolate,** $[Pt\{S(CH_2.COOK)_2\}_2I_2]$, represented by the acid, and by **platinous diiodobispotassiumthiodiglyeolate,** $[Pt\{S(CH_2COOK)_2\}_2I_2]$; N. S. Kurnakoff, **platinous quaterthiocarbamidoiodide,** $Pt\{CS(NH_2)_2\}_4]I_2$; P. Klason, **platinous iodoethylmercaptidodiammine,**

$[Pt(NH_3)_2(SC_2H_5)I]$; L. Ramberg prepared platinous diiodobisbenzonitrile, $[Pt(C_6H_5.CN)_2I_2]$, and he prepared **platinous diiodobisphenylcarbylamine,** $[Pt(C_6H_5.NC)_2I_2]$ and **platinous triiodophenylcarbylamine,** $[Pt(C_6H_5NC)I_3]$; G. Wallin, **platinous diiodobisamidoacetate,** $[Pt(NH_2.CH_2.COOH)_2I_2]$; P. Klason, **platinous iodomercaptanodiammine,** $[Pt(NH_3)(C_2H_5S)I]$; L. A. Tschugaeff and co-workers prepared **platinous methylcarbylaminehydrazinoiodide,** $[(CH_3NC)_2Pt(N_2H_3)_2Pt(CH_3NC)_2]I_2$; and **platinous ethylcarbylaminohydrazinoiodide,** $[(C_2H_5NC)_2Pt(N_2H_3)_2Pt(C_2H_5NC)_2]I_2$. J. Petren prepared **platinous diiodobisethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2I_2]$, **platinous diiodopyridineethylselenine,** $[Pt(C_5H_5N)\{(C_2H_5)_2Se\}I_2]$, and **platinous diiodoethylsulphineethylselenine,** $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}I_2]$; H. Löndahl, **platinous bisethylenesulphineiodide,** $[Pt\{(C_2H_4)_2S_2\}]I_2$; and R. Bunsen, and K. A. Jensen and E. Frederiksen, **platinous diiodocacodyloxide,** $[Pt\{As_2(CH_3)_4O\}I_2]$. K. A. Jensen studied the dipole moments of some iodosulphines, and of the phosphines; he also prepared the cis- and trans- **platinous diiodobistriethylphosphines,** $[Pt\{(C_2H_5)_3P\}_2I_2]$; and trans- **platinous diiodobistriethylstibine,** $[Pt\{(C_2H_5)_3Sb\}_2I_2]$.

R. Klement prepared **potassium iodoplatinite,** K_2PtI_4, analogous with the chloroplatinite and gave 172·5 for the mol. vol.

According to R. J. Kane, when a dil. aq. soln. of platinic chloride is mixed with an excess of potassium iodide, and the precipitate washed free from potassium chloroplatinate by hot water, and then dried, there remains black **platinosic iodide,** or **platinum triiodide,** PtI_3. G. Clementi used warm soln. R. Klement gave 7·414 for the sp. gr. at 25°/4° and 77·7 for the mol. vol. R. J. Kane observed that the tiiodide gives off iodine at 121°, and all the iodine is expelled below redness. Cold water has no action on the salt, but boiling water extracts some iodine. Cold hydrochloric, sulphuric, and nitric acid have no action on the salt. An aq. soln. of potassium iodide and hydriodic acid dissolve the salt to form a wine-red soln. Aq. ammonia colours the salt green, brown, and red. Alcohol, and ether have no action on the salt. Potash lye dissolves the salt forming a yellowish soln. which becomes pale red when neutralized with nitric acid, and colourless with an excess of acid. The alleged triiodide is thought to be a mixture of platinous and platinic iodides formed by the partial decomposition of the platinic iodide by the hot water.

P. T. Cleve reported a number of what may be platinosic iodoammines. For instance, **platinosic ennealodoctammine,** $7PtI_2.PtI_4.16NH_3$, or $Pt_4(NH_3)_8I_9$, was obtained as a black powder by the action of soda lye on **platinosic pentaiodotetrammine,** $Pt_2(NH_3)_4I_5$, or $3PtI_2.PtI_4.8NH_3$, which was obtained by the action of hydriodic acid on **platinosic hexaiodotetrammine,** $Pt_2(NH_3)_4I_6$, or $Pt_2I_6.4NH_3$, obtained by boiling platinic tetraiododiammine with hydriodic acid. G. T. Morgan and F. H. Burstall prepared complexes with dipyridyl.

The **platinous chloroiodides** are represented by some complex salts. O. Carlgren and P. T. Cleve prepared **platinous dichlorodiamminochloroiodide,** $[Pt(NH_3)_2Cl_2]ICl$. H. Londahl obtained **platinous iodoethylenesulphineamminoiodochloroplatinite,** $[Pt(NH_3)\{(C_2H_4)_2S_2\}I]I.PtCl_2$; C. Rudelius **platinous cis-chloroiodobispropylsulphine;** $[Pt\{(C_3H_7)_2S\}ClI]$; and J. Petren, **platinous chloroiodobisethylselenine,** $[Pt\{(C_2H_5)S\}_2ClI]$; and **platinous chloroiodoethylsulphine-ethylselenine,** $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}ClI]$; J. Petren also reported **platinous bromoiodobisethylselenine,** $[Pt\{(C_2H_5)_2S\}_2BrI]$.

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§ 26. Platinic Iodide

L. Wöhler and F. Müller[1] obtained **platinous iodide, or platinum diiodide,** PtI_2, by heating the triiodide above 400° in a sealed tube. H. D. K. Drew and co-workers prepared **platinous diamminodiiodide,** $[Pt(NH_3)_2I_2]$, by the action of an excess of an aq. soln. of an alkali halide on a soln. of the corresponding chloride ; or by the action of hydriodic acid on the base. The α-salt is a pale yellow crystalline powder ; and the β-salt forms orange-yellow, prismatic needles, and gives a reddish-brown colouration with phenoxtellurine disulphate. L. Wöhler and F. Müller obtained **platinum triiodide,** PtI_3, by heating the tetraiodide at 350° to 400° in a sealed tube. Their observations on the range of stability of the iodides are summarized in Fig. 91.

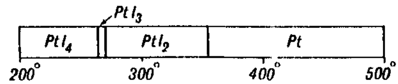

FIG. 91.—Range of Stability of the Platinum Iodides.

J. L. Lassaigne found that when spongy platinum is heated with iodine at ordinary press., union is incomplete. No **platinic iodide, or platinum tetraiodide,** PtI_4, is formed when spongy platinum is heated with iodine and water, and with a mixture of hydriodic and nitric acids, but G. Clementi obtained platinic iodide by heating finely-divided platinum with iodine in a sealed glass tube below the temp. of dissociation of the tetraiodide. L. Wöhler and F. Müller obtained the anhydrous tetraiodide by heating platinum with iodine in a sealed tube at 240° to 300° ; the triiodide is formed at 350° to 400° ; and the diiodide at a higher temp. W. Pullinger prepared platinic iodide by dissolving platinum in a soln. of iodine in hydriodic acid, evaporating the liquid to dryness, heating the residue in an air-bath at 180°, and washing the product with water. G. Clementi obtained the iodide by the action of hydriodic acid on hydrated platinic oxide ; J. L. Lassaigne, by boiling a mixture of dil. soln. of platinic chloride, free from acid, and of potassium iodide, and washing and drying the precipitate. L. Pigeon employed 4 mols. of potassium iodide to 1 mol. of platinic chloride, or adding the theoretical proportion of potassium iodide soln. to hydrochloroplatinic acid. H. Töpsöe recommended this process. I. Bellucci warmed on the water-bath a mixture of a soln. of hydrochloroplatinic acid or magnesium chloroplatinate and a small excess of hydriodic acid. The precipitate was washed by decantation with boiling water, collected on a filter-paper, and dried at 100°.

J. L. Lassaigne said that the black precipitate is flocculent and amorphous, or crystalline ; it has no smell or taste. R. Klement gave 6·064 for the sp. gr. at 25°/4°, and 115·9 for the mol. vol. L. Pigeon observed that platinic iodide gives off iodine at ordinary temp.—1·4 per cent. loss was observed in 24 hrs. ; H. Töpsöe said that very little iodine is lost at 100° ; and J. L. Lassaigne found that iodine vapour is developed at 130°, and platinum finally remains. W. Pullinger found that the iodine is not completely removed from platinic iodide by molten sodium carbonate. L. Pigeon gave for the heat of formation with gaseous iodine, $(Pt, 2I_2)$ $=39·0$ Cals., and with solid iodine 17·4 Cals. F. Jez found the thermionic emission

of platinum in iodine vapour is greater than in air due, it is suggested, to the formation of a film of platinic iodide which is responsible for the emission. According to E. H. Archibald and W. A. Patrick, the mol. electrical conductivity in alcohol, in mhos at 25° increases with dilution and attains a constant value at dilutions of about 600 litres. The conductivity increases rapidly with time as indicated in Fig. 92, but constancy is attained in about 25 hrs. at 25°. The increase is attributed to a reaction involving the formation of a substance having a large conductivity in the alcohol. With methyl alcohol soln. the conductivity is rather greater than it is in soln. with ethyl alcohol, but similar variations with time and concentration occur. J. L. Lassaigne observed that platinic iodide is insoluble in water, and is not decomposed by boiling with water. Chlorine-water forms hydrochloroplatinic acid, and may be chlorine iodide. Platinic iodide combines with other iodides to form crystalline iodoplatinates; H. Töpsöe found that the salt is soluble in soln. of alkali iodides, but not so readily in soln. of other iodides. W. Manchot and G. Lehmann observed that in carbon monoxide, the halogen is displaced at a lower temp. than it is in an indifferent gas, and no carbonyl iodide is formed. According to F. Field, the rose colour of a soln. of platinic and potassium iodides is destroyed by soln. of urine, albumin, tannic acid, gallic acid, pyrogallic acid, potassium cyanide or thiocyanate, the liquid in which animal or vegetable substances have been boiled, and saliva; but not by urea, uric acid, starch, dextrin, cane-sugar, grape-sugar, glycerol, gelatin, oxalic acid, tartaric acid, citric acid, acetic acid, carbon disulphide, and alcohol. H. Töpsöe noted that sulphurous acid converts the iodide into platinous sulphite. J. L. Lassaigne found that cold, conc. sulphuric acid does not act on the iodide, but when heated, iodine is evolved. R. J. Kane observed that ammonia converts the salt into the oxyiodide, $PtOI_2.2NH_3.H_2O$, and H. Töpsöe showed that an ammine is formed when platinic iodide is dissolved in aq. ammonia. I. Bellucci found that platinic iodide forms a green soln. with alcohol, and some of the iodide is decomposed; the salt dissolves in 95 per cent. alcohol without decomposition at ordinary temp., but in light the salt is slowly decomposed. A. Schleicher and W. Schmitz prepared **platinous bisethylenediaminoiodide,** $[Pt\,en_2]I_2$, and found that dil. sulphuric acid converts it into $[(H_2O)-Pt(en)_2-(H_2O)_5I(H_2O)_5-Pt(en)_2-(H_2O)]I.5H_2O$.

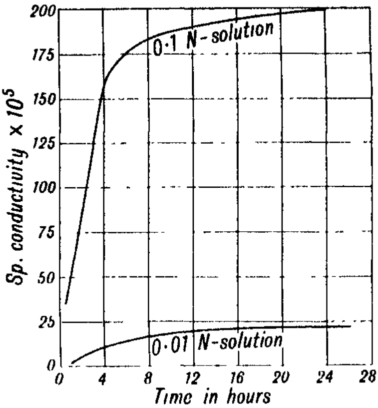

FIG. 92.—The Electrical Conductivity of Solutions of Platinic Iodide in Ethyl Alcohol.

P. T. Cleve prepared **platinic diiodotetramminoiodide,** $[Pt(NH_3)_4I_2]I_2$, by the action of an excess of potassium iodide on the corresponding dichloro-nitrate; by the action of iodine on platinous tetramminoiodide; and by the action of potassium triiodide on platinous tetramminochloride. The black scales recall graphite, the salt also occurs in dark brown, translucent plates. The salt decomposes at 130° to 140°. A. R. Klien studied the action of water, acids, and alkaline soln. According to P. T. Cleve, the salt is soluble in water, particularly boiling water; mercury reduces it to platinous tetramminoiodide; silver nitrate slowly precipitates all the iodine from the aq. soln. and a boiling soln. of an ammonium salt partially converts it into **platinic diiodohexammino-μ-diamineiodide,** $[I(NH_3)_3Pt(NH_2)_2Pt(NH_3)_3I]I_4$. The diiodotetramminoiodide also forms lemon-yellow needles of **platinic diiodotetramminoiodomercurate,** $[Pt(NH_3)_4I_2](HgI_3)_2$. P. T. Cleve prepared **platinic trans-tetraiododiammine,** $[Pt(NH_3)_2I_4]$, by the action of tincture of iodine on platinous diiododiammine. The black, amorphous powder passes into the diiodohexammino-μ-diamineiodide when it is boiled with aq. ammonia; boiling, conc. potash lye

colours the salt orange-yellow, but little or no ammonia is evolved; and acids yield a black product. P. T. Cleve obtained **platinic diiodohexammino-μ-diimido-iodide,** $[I(NH_3)_3Pt(NH)_2Pt(NH_3)_3I]I_2.H_2O$, by boiling platinic diiodotetrammino-iodide with aq. ammonia. The chrome-yellow, rhombic plates furnish silver iodide when treated with silver nitrate; and nitric acid forms iodonitroxyltetrammino-nitrate. S. M. Jörgensen obtained **platinic cis-tetraiododiammine,** by the action of potassium iodide on the cis-tetrachlorodiammine. The crystals resemble those of iodine. P. T. Cleve reported **platinic hexaiododiammine,** $[Pt(NH_3)_2I_4(I_2)]$, to be formed by the action of a hot tincture of iodine on the cis-tetraiodotetrammine. The black powder consists of hexagonal dark purple-red plates. Alkali lye colours the salt brown, then cinnabar-red, and when heated, ammonia is evolved and the colour becomes yellow. L. A. Tschugaeff and co-workers prepared **platinic hydrazinocarbylaminoiodide.**

W. J. Pope and S. J. Peachey described **platinic iodotrimethylaminodiammine,** $[Pt(NH_3)_2(CH_3)_3NI]$; F. G. Mann and W. J. Pope reported **platinic dichloro-$\beta\beta'\beta''$-triaminotriethylamino-iodide,** $[PtN(C_2H_4.NH_2)_3Cl_2]I_2$. R. L. Datta, **platinic bismethylaminehydroiodide,** $2CH_3NH_2.HI.PtI_4$; **platinic bisdimethylaminehydroiodide,** $2(CH_3)_2NH.HI.PtI_4$; **platinic bistrimethyl-aminehydroiodide,** $2(CH_3)_3N.HI.PtI_4$; **platinic bistetramethylammoniumiodide,** $2(CH_3)_4NI.PtI_4$; **platinic bisethylaminehydroiodide,** $2C_2H_5NH_2.HI.PtI_4$; **platinic bisdiethylaminehydroiodide,** $2(C_2H_5)_2NH.HI.PtI_4$; **platinic bistriethylaminehydroiodide,** $2(C_2H_5)_3N.HI.PtI_4$; **platinic bis-tetraethylammoniumiodide,** $2(C_2H_5)_4NI.PtI_4$; **platinic bisdipropylaminehydroiodide,** $2(C_3H_7)_2NH.HI.PtI_4$; and **platinic bistetrapropylammoniumiodide,** $2(C_3H_7)_4NI.PtI_4$; R. L. Datta and T. Ghosh, **platinic methylethylpropylphenylammoniumiodide,** $(CH_3)(C_2H_5)(C_3H_7)(C_6H_5)NI.PtI_4$. A. P. Smirnoff prepared **platinic trispropylenediaminoiodide,** $[Pt(C_3H_6.N_2H_4)_3]I_4$, in its racemic, dextro- and laevo-forms. R. L. Datta obtained **platinic bisallylaminehydro-iodide,** $2C_3H_5NH_2.HI.PtI_4$; **platinic bisanilinehydroiodide,** $2C_6H_5NH_2.HI.PtI_4$; and **platinic bispyridinehydroiodide,** $2(C_5H_5N).HI.PtI_4$; S. G. Hedin described **platinic tetraiodobispyridine,** $[Pt(C_5H_5N)_2I_4]$; S. M. Jörgensen, **platinic diiodobispyridinediamminoiodide,** $[Pt(NH_3)_2(C_5H_5N)_2I_2]I_2$, by the action of an excess of a soln. of iodine and potassium iodide on platinous bispyridinediamminochloride in two forms according as the cis- or trans-platinous salt is employed. R. L. Datta prepared **platinic bis-α-picolinehydroiodide,** $2C_6H_7N.HI.PtI_4$; R. L. Datta and T. Ghosh, **platinic bispiperidinehydroiodide,** $2C_5H_{11}N.HI.PtI_4$; and **platinic bisquinolinehydroiodide,** $2C_9H_7N.HI.PtI_4$, with ordinary and iso-quinoline. G. Wallin reported **platinic tetraiodobisamidoacetate,** $[Pt(NH_2CH_2COOH)_2I_4]$; and **platinic diiodobis-glycine,** $[Pt(NH_2.CH_2.COO)_2I_2]$.

C. Enebuske described **platinic tetraiodobismethylsulphine,** $[Pt\{(CH_3)_2S\}_2I_4]$; R. L. Datta, **platinic bistrimethylsulphoniumiodide,** $2(CH_3)_3SI.PtI_4$; C. W. Bomstrand, and C. Rudelius, **platinic tetraiodobisethylsulphine,** $[Pt\{(C_2H_5)_2S\}_2I_4]$; R. L. Datta, **platinic bistriethylsul-phoniumiodide,** $2(C_2H_5)_3SI.PtI_4$; C. Rudelius, and M. Weibull, **platinic tetraiodobis-i-propylsulphine,** $[Pt\{(C_3H_7)_2S\}_2I_4]$; H. Londahl, **platinic tetraiodobis-i-butylsulphineiodide,** $[Pt\{(C_4H_9)_2S\}_2I_4]I_2$; J. Petren, **platinic tetraiodobisethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2I_4]$; and **platinic tetraiodoethylselenine,** $[Pt\{(C_2H_5)_2\}\{(C_2H_5)_2Se\}I_4]$.

According to J. L. Lassaigne, cold, dil. hydriodic acid in contact with platinic iodide for, say, 24 hrs., forms a red soln. which when evaporated in vacuo, or over lime yields crystals of **hydriodoplatinic acid,** $H_2PtI_6.9H_2O$. J. L. Lassaigne thought that the crystals were anhydrous, but H. Töpsöe showed that the solid so formed is the *enneahydrate*. J. L. Lassaigne said that the reddish black, deliquescent, acicular crystals are odourless, and have an astringent, somewhat acidic, taste. H. Töpsöe showed that the six-sided plates are monoclinic, and show twinning. The faces of the crystals lose their metallic lustre when exposed to air, and acquire a black film of platinic iodide owing to the loss of hydrogen iodide. J. L. Lassaigne found that in a dry vacuum, the crystals evolve a little hydrogen iodide, and more so at 100°; at a higher temp., hydrogen iodide and iodine are evolved and platinum remains. The compound is freely soluble in water, and when the wine-red soln. is diluted with a large proportion of water, platinic iodide is deposited, and more quickly if the aq. soln. be exposed to sunlight, or, according to H. Töpsöe, if heated. J. L. Lassaigne said that chlorine decomposes the aq. soln. with the deposition of iodine, and platinic iodide; and alkali lye forms alkali iodides. Hydriodoplatinic acid forms a series of salts, the **iodoplatinates.** H. I. Schlesinger and R. E. Palmateer discussed the relative stability of the halogenoplatinates.

J. L. Lassaigne prepared **ammonium iodoplatinate,** $(NH_4)_2PtI_6$, by digesting at a gentle heat a soln. of platinic iodide and ammonium iodide, and evaporating the red liquid. H. Töpsöe recommended evaporating the soln. over calcium oxide. J. L. Lassaigne's analysis corresponds with $(NH_4)PtI_5$, but the analyses of H. Töpsöe, and R. L. Datta correspond with $(NH_4)_2PtI_6$. R. L. Datta prepared the salt by adding an excess of a soln. of ammonium iodide, gradually, with agitation, to a 10 per cent. soln. of hydrochloroplatinic acid, washing the product with a little water and dil. alcohol, and drying in a desiccator. J. L. Lassaigne observed that the black, four-sided plates are stable in air; H. Töpsöe said that the octahedral crystals belong to the cubic system, and that the habit is not changed if an excess of ammonium iodide be present in the mother-liquid. The sp. gr. is 4·61, and the mol. vol. 216·0. R. L. Datta observed that when the salt is heated, iodine is evolved, then white clouds of ammonium iodide, and finally platinum remains. The salt forms a dark-red soln. with water, and the aq. soln. gradually deposits platinic iodide. The salt is insoluble in a sat. soln. of ammonium iodide; and in alcohol.

J. L. Lassaigne prepared **potassium iodoplatinate,** K_2PtI_6, by allowing a soln. of platinic iodide and potassium iodide to crystallize, and washing the crystals with alcohol of sp. gr. 0·843 to remove admixed potassium iodide. W. W. Mather, and H. Töpsöe used a similar process. R. L. Datta added 10 per cent. hydrochloroplatinic acid, with agitation, to a sat. soln. of potassium iodide, washed the crystals with a little water on a suction-filter, and then with alcohol. R. J. Kane used a similar process but added some ether to the soln. The black, rectangular plates were shown by H. Töpsöe to belong to the cubic system, and by recrystallizing in the presence of an excess of potassium iodide he obtained cubes, and from aq. soln., octahedra. The sp. gr. given by C. H. D. Boedeker is 5·176; by H. Töpsöe, 5·031; and R. Klement gave 4·963 for the sp. gr. at 29°/4°, and 208·5 for the mol. vol. H. I. Schlesinger and M. W. Tapley studied the absorption spectrum; and H. I. Schlesinger and R. E. Palmateer, the relative stabilities of the halogen salts. J. L. Lassaigne observed that a part of the iodine is lost at 100°. The salt is readily soluble in water forming a deep wine-red soln. Very dil. soln. were found by J. L. Lassaigne, and W. W. Mather to deposit platinic chloride, particularly when exposed to light. The salt is not decomposed by conc. sulphuric acid. M. Vézes showed that with a boiling soln. of potassium nitrite, potassium nitritoplatinite is formed. J. L. Lassaigne said that the salt is insoluble, or very sparingly soluble in absolute alcohol. R. L. Datta prepared **rubidium iodoplatinate,** Rb_2PtI_6, by the action of a conc. soln. of rubidium iodide on hydrochloroplatinic acid. The black crystals are soluble in water; and similarly also with **cæsium iodoplatinate,** Cs_2PtI_6.

J. L. Lassaigne prepared **sodium iodoplatinate,** $Na_2PtI_6.6H_2O$, from a soln. of platinic iodide and sodium iodide; and H. Töpsöe, by treating hydrochloroplatinic acid with an excess of sodium iodide, and evaporating the liquid at ordinary temp. over sulphuric acid. The lead-grey, striated needles were found by J. L. Lassaigne to be deliquescent, and H. Töpsöe said the brown prisms are not deliquescent, and that they are probably monoclinic, and that twinning occurs, about the (100)-face. The sp. gr. is 3·707, and the mol. vol. 300·4. L. Pigeon found that the heat of formation in an excess of a soln. of sodium iodide is $(PtI_4, 2NaI)=7{\cdot}3$ Cals. The faces of the crystals become matte on exposure to air. J. L. Lassaigne said that the salt is freely soluble in water and in alcohol.

H. Töpsöe prepared **calcium iodoplatinate,** $CaPtI_6.12H_2O$, by evaporating over sulphuric acid, a soln. of an excess of calcium iodide in hydrochloroplatinic acid. The rhombohedral crystals are not deliquescent, and dissolve freely in water, and in alcohol. J. L. Lassaigne obtained **barium iodoplatinate,** $BaPtI_6.nH_2O$, by slowly evaporating a soln. of platinic iodide and barium iodide. The deliquescent crystals resemble those of the sodium salt.

H. Töpsöe obtained **magnesium iodoplatinate,** $MgPtI_6.9H_2O$, by evaporating, over sulphuric acid, a soln. of an excess of magnesium iodide in hydrochloroplatinic

acid. The trigonal crystals have the axial ratio $a : c = 1 : 1\cdot8700$, and $\alpha = 72° 6'$; the sp. gr. is 3·458; and the mol. vol. 302·3. H. Töpsöe obtained **zinc iodoplatinate,** $ZnPtI_6.9H_2O$, from a soln. of platinic and zinc iodides; and by evaporating, over sulphuric acid, a soln. of an excess of zinc iodide in hydrochloroplatinic acid. The trigonal crystals resemble those of the magnesium and manganese salts; the axial ratio is $a : c = 1 : 1\cdot8685$, and $\alpha = 72° 13'$; the sp. gr. is 3·689; and the mol. vol. 321·7. J. L. Lassaigne also prepared the deliquescent crystals and said that they have an astringent taste. *Vide supra*, for **platinic tetramminoiodomercurate,** $[Pt(NH_3)_4](HgI_3)_2$.

H. Töpsöe prepared **manganese iodoplatinate,** $MnPtI_6.9H_2O$, by evaporating spontaneously, over sulphuric acid, a soln. of an excess of manganese iodide in hydrochloroplatinic acid. The trigonal crystals have the axial ratio $a : c = 1 : 1\cdot8685$, and $\alpha = 72° 8'$; the sp. gr. is 3·604; and the mol. vol., 326·4. E. Herlinger gave 352·7 for the mol. vol. of the hexahydrate. J. L. Lassaigne obtained **ferrous iodoplatinate,** $FePtI_6.9H_2O$, by evaporating a soln. of platinum and ferrous iodides; and H. Töpsöe, by evaporating, over sulphuric acid, a soln. of ferrous iodide in an excess of hydrochloroplatinic acid. The trigonal crystals have the axial ratio $a : c = 1 : 1\cdot8675$, and $\alpha = 72° 11'$; the sp. gr. is 3·455; and the mol. vol. 340·8. E. Herlinger gave 340·0 for the mol. vol. of the hexahydrate. The deliquescent crystals acquire a film of ferric hydroxide on exposure to air. H. Töpsöe prepared **cobalt iodoplatinate,** $CoPtI_6.9H_2O$, by evaporating, over sulphuric acid, a soln. of an excess of cobalt iodide in hydrochloroplatinic acid. The trigonal crystals of the *enneahydrate* have the axial ratio $a : c = 1 : 1\cdot8757$, and $\alpha = 72° 2'$; the sp. gr. 3·618; and mol. vol. 326·2. On exposure to air, the faces of the crystals become matte, owing to the loss of iodine. Trigonal crystals of the *dodecahydrate* are also obtained. The sp. gr. is 3·048, and the mol. vol. 408·1. E. Herlinger gave 325·5 for the mol. vol. H. Töpsöe also prepared **nickel iodoplatinate,** $NiPtI_6.6H_2O$, by crystallization from a hot, sat. soln. of an excess of nickel iodide in hydrochloroplatinic acid, or by evaporating the soln. spontaneously at ordinary temp. The green crystals of the *hexahydrate* are trigonal with the axial ratio $a:c = 1 : 0\cdot5186$, and $\alpha = 112° 18'$; W. Biltz found that the sp. gr. is 3·976, and the mol. vol. 283·2. The crystals are slightly deliquescent, and soon lose their lustre on exposure to air. They dissolve in water with decomposition. The *enneahydrate* is obtained by spontaneously evaporating at ordinary temp., a soln. with the theoretical proportions of hydrochloroplatinic acid and nickel iodide. The trigonal crystals have the axial ratio $a : c = 1 : 1\cdot8788$, and $\alpha = 71° 55'$. The crystals are isomorphous with the corresponding salts of magnesium, zinc, manganese, iron, and cobalt. The sp. gr. is 3·549; and the mol. vol. 332·5. E. Herlinger gave 331·8 for the mol. vol. The crystals are deliquescent, and lose iodine on exposure to air. The salt is decomposed when it dissolves in water.

I. Bellucci obtained **dihydroxytetraiodoplatinic acid,** $H_2Pt(OH)_2I_4$, in soln. by allowing platinic iodide to remain in contact with 95 per cent. alcohol. The soln. has an acidic reaction; decomposes carbonates; and gives precipitates of **dihydroxytetraiodoplatinates** when treated with soluble salts of the metals. By adding a small excess of a 10 per cent. soln. of silver nitrate to an alcoholic soln. of platinic iodide, washing the dark red precipitate with water, and drying it in vacuo, **silver dihydroxytetraiodoplatinate,** $Ag_2Pt(OH)_2I_4$, was formed. With a conc. soln. of mercuric chloride in the presence of sodium acetate, there was formed red **mercuric dihydroxytetraiodoplatinate,** $HgPt(OH)_2I_4$; with a conc. soln. of thallous acetate, brick-red **thallous dihydroxytetraiodoplatinate,** $Tl_2Pt(OH)_2I_4$; and with lead acetate greyish-red **lead dihydroxytetraiodoplatinate,** $PbPt(OH)_2I_4$. F. Reiff also discussed the silver and thallous salts.

R. J. Kane in his study of the action of ammonia on platinic iodide reported the formation of **platinic dioxytetraiodotetrammine,** $Pt_2(NH_3)_4O_2I_4$, or $PtOI_2.2NH_3.H_2O$; O. Carlgren and P. T. Cleve obtained **platinic dihydroxytetramminoiodide,** $[Pt(NH_3)_4(OH)_2]I_2$; E. Koefoed, **platinic hydroxyiodotetrammino-**

iodide, $RI_2[Pt(NH_3)_4(OH)I]I_2$; and L. A. Tschugaeff, **platinic diiodotetrammino-iodide,** $[Pt(NH_3)_4I_2]I_2$.

W. J. Pope and S. J. Peachey prepared **trimethyl platinic iodide,** $(CH_3)_3PtI$, by the action of Grignard's reagent—magnesium methyliodide—on hydrochloroplatinic acid: $PtCl_4+3(CH_3)MgI=(CH_3)_3PtI+2MgCl_2+MgI_2$. When heated with a mixture of benzene, alcohol, and conc. ammonia, it forms **trimethyl platinic diamminoiodide,** $Pt(CH_3)(NH_3)_2I$.

Several mixed halides have been reported. H. Kämmerer dissolved platinum with 4 gram-atoms of iodine in aqua regia, evaporated the soln. on a water-bath and allowed it to cool over sulphuric acid; the brick-red, deliquescent prisms of **platinic dichlorodiiodide,** $PtCl_2I_2$, which are formed melt below 100°. Potassium or ammonium chloride precipitates the chloroplatinate whilst iodides remain in soln.; potassium iodide colours the soln. deep red; and iodine chloride forms platinic chloride and iodine. W. W. Mather reported **platinic chlorotriiodide,** $PtClI_3$, to be formed by evaporating to dryness a mixture of hydrochloroplatinic acid and hydriodic acid, and heating the residue to 149° when hydrogen chloride and iodide, and iodine chloride escape. H. Töpsöe added that if too large an excess of hydriodic acid is employed some hydroiodoplatinous acid is formed. The black powder gives off iodine and iodine chloride when heated between 205° and 315°, and spongy platinum remains. The salt is insoluble in water, and behaves towards sulphur dioxide, alkali sulphites, and ammonia like platinic iodide; it is sparingly soluble in alcohol, and forms a red soln. with potash lye, from which sulphuric acid precipitates the chlorotriiodide unchanged. P. T. Cleve, and O. Carlgren and P. T. Cleve prepared **platinic chloroiodotetramminochloride,** $[Pt(NH_3)_4ClI]Cl_2$, by the action of hydrochloric acid on the nitrate or sulphate of the diiodohexammino-μ-diamine.

C. Enebuske prepared **platinic dichlorodiiodobismethylsulphine,** $[Pt\{(CH_3)_2S\}_2Cl_2I_2]$; H. Löndahl, **platinic dichlorodiiodobisbutylsulphine,** $[Pt\{(C_4H_9)_2S\}_2Cl_2I_2]$, with iso- and secondary butyl; J. Petren, **platinic dichlorodiiodobisethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2Cl_2I_2]$, and **platinic chlorotriiodobisethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2ClI_3]$; and A. Cahours and H. Gal, **platinic dichlorodiiodobisethylphosphine,** $[Pt\{P(C_2H_5)_3\}_2Cl_2I_2]$.

The **platinic bromoiodides** are represented by **platinic dibromodiiodomethylsulphine,** $[Pt\{(CH_3)_2S\}_2Br_2I_2]$, prepared by C. Enebuske; J. Petren described **platinic tribromoiodobisethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2Br_3I]$, **platinic dibromodiiododiethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2Br_2I_2]$, **platinic bromotriiododiethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2BrI_3]$, **platinic dibromodiiododiethylsulphinodiethylselenine,** $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}Br_2I_2]$; and G. Wallin, **platinic dibromodiiodobisamidoacetate,** $[Pt(NH_2.CH_2.COOH)_2Br_2I_2]$. J. Petren prepared **platinic diiododinitritoethylsulphinoethylselenine,** $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}(NO_2)_2I_2]$.

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§ 27. Platinum Sulphides

C. Ridolfi [1] utilized the fact that sulphur does not attack platinum but attacks the base metals to separate platinum from impurities. R. A. Cooper obtained a mineral whose composition be represented by $Pt(As, S)_2$, in the residue left after the action of aqua regia on the platiniferous norites of Bushveld, Transvaal. The mineral was called **cooperite**. R. A. Cooper later reported that the arsenic was present as an impurity in the form of sperrylite, and he changed the formula to PtS_2. H. Schneiderhöhn, and H. R. Adam made observations on the mineral on the assumption that it is platinum disulphide. F. A. Bannister showed that the analyses agree better with the formula PtS. H. R. Adam studied the mineral.

E. Davy prepared **platinous sulphide, or platinum monosulphide,** PtS, by heating to redness a mixture of sulphur and spongy platinum in an evacuated glass tube; but F. Rössler could not obtain the sulphide as a fused regulus. G. Preuner observed the formation of the sulphide in small proportions when gaseous sulphur acts on platinum at 950° to 1240°; L. Thomassen, by heating stöichiometrical proportions of the two elements in a quartz tube; H. G. Krall, and L. Wöhler and co-workers, by heating the disulphide at 630°; J. Uhl, superficially by passing sulphur dioxide over heated platinum; and W. Skey, by contact of hydrogen sulphide or ammonium sulphide whereby the metal acquires a film and so resists amalgamation. H. St. C. Deville and H. Debray obtained the sulphide by melting metal with ten times its weight of pyrite under borax at a red-heat, and washing the product first with cold and then with hot, conc. hydrochloric acid; R. Schneider, by heating a higher sulphide in a current of carbon dioxide; R. Böttger, by igniting oxidized platinum sulphide in a platinum crucible until it takes fire with a loud hissing noise, allowing the crucible to cool whilst the contents are protected from air, boiling the residue with aqua regia, washing the product, and drying it in vacuo; L. N. Vauquelin, by igniting ammonium chloroplatinate with twice its weight of sulphur in a closed crucible, and also by heating the same salt with an equal weight of sulphur and ignited sodium carbonate and washing away the sodium sulphide by water—*vide infra*, Pt_4S_5; J. J. Berzelius, by decomposing platinous chloride with an alkali sulphide; and W. Knop, C. Himley, and H. Vohl, by boiling a soln. of platinic chloride with an excess of sodium thiosulphate until the liquid is deep red, adding a large proportion of water, then hydrochloric acid, and keeping warm for a long time nearly at 100° until the evolution of sulphur dioxide has ceased. The liquid is then colourless, and there is a grey precipitate of platinous sulphide mixed with sulphur—the latter is easily removed by washing with a suitable solvent. A. Voet prepared the colloidal sulphide.

According to L. N. Vauquelin, platinous sulphide is a dull, lead-grey powder which acquires a metallic lustre when rubbed on paper; it also occurs as a shining

black powder; or in slender, black, lustrous needles. According to F. A. Bannister, the X-radiograms of cooperite, PtS, show that the tetragonal crystals have a face-centred unit cell with edges a=4·91 A., and c=6·10 A., or $a:c$=1 : 1·242; and the values for synthetic platinous sulphide are a=4·92 A., and c=6·12 A.; the unit cell contains four PtS-molecules with planar PtS_4-groups, and tetrahedral PtS_4-groups. The shortest distance between the platinum and sulphur atoms is 2·32 A.; between the sulphur atoms, 3·05 A.; and between the platinum atoms, 3·47 A. L. Pauling and M. L. Huggins discussed this subject. The sp. gr. of cooperite is 10·2, and of synthetic platinous sulphide, 10·1. W. Biltz and R. Juza gave 10·04 for the sp. gr.; and 22·6 for the mol. vol. E. Davy's value 6·2 for the sp. gr. is too low. When platinous sulphide is heated in a closed vessel, it shows signs of fusion. W. Biltz and R. Juza measured the isothermal decomposition and the results are summarized in Fig. 93. The sulphide is slightly miscible with platinum, but there is no indication of subsulphides. The heat of formation from solid rhombic sulphur is (Pt, S)=16 Cals. J. N. Frers studied the combination PtS—ZnO as a radio-detector.

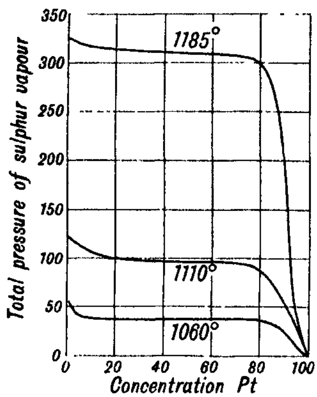

FIG. 93.—Isothermal Decomposition of Platinum Monosulphide.

F. A Bannister found a mineral in the platiniferous ore of Rustenburg, Transvaal, which he called **braggite**—after W. H. Bragg. It contains about 5 per cent. of nickel, 20 per cent. of palladium, 19 per cent. of sulphur, and 58 per cent. of platinum; its composition approximates (Pt,Pd,Ni)S. The crystals are tetragonal prisms, and the X-radiograms correspond with a unit cell with a=6·37 A., and c=6·58 A. Each cell contains eight (Pt,Pd,Ni)S-molecules. The sp. gr. is 8·63, and the value calculated from the lattice constants is 8·9.

E. Davy said that the compound is a non-conductor of electricity. R. Böttger found that at 19°, hydrogen reduces the sulphide to spongy platinum. E. Davy observed that the sulphide is stable in air, and when heated in air, it forms the metal. A. Mailfert observed that with ozone there is formed some sulphuric acid. B. Aulenkamp studied the sensitiveness of the sulphide to light. E. Davy observed that the sulphide is not attacked by water, and it is scarcely attacked by boiling mineral acids, or boiling aqua regia. R. Böttger said that in air, platinous sulphide acts on alcohol like platinum black, but less vigorously. R. Böttger, and H. St. C. Deville and H. Debray showed that the sulphide is not attacked by boiling potash lye; and J. Ribau, that it is almost insoluble in alkali sulphides. E. Davy observed that the sulphide is decomposed when heated with zinc filings, or with potassium chlorate; and R. Böttger also found that fused potassium nitrate acts similarly. H. Löndahl observed the possible formation of **platinous sulpho-bis-i-butylsulphine**, $[Pt\{(C_4H_9)_2S\}_2S]$, as a brown, oily precipitate, by the action of potassium sulphide on a soln. of the corresponding sulphate. F. Mylius and F. Förster prepared **platinous sulphocarbonyl**, $[Pt(CO)S]_2$, and a complex with $2H_2S$; and V. N. Ivanoff, **platinum bisthiocarbamidotetrahydroxysulphide**, $Pt_4(OH)_4S\{CS(NH_2)\}_2$. A number of platinous halogen-sulphines and thio-salts have been described in connection with the platinum halides.

R. Schneider observed the formation of **potassium sulphoplatinite**, $K_2S.PtS$, or K_2PtS_2, but was unable to isolate the salt. He prepared **potassium stannic sulphoplatinite**, $K_2S.3PtS.SnS_2$, by melting 1 part of spongy platinum with 2 parts of stannic sulphide, 6 to 8 parts of dry potassium carbonate, and 6 to 8 parts of sulphur, and found that when this salt is heated to dark redness in a current of hydrogen, it loses sulphur as hydrogen sulphide to form a mixture of platinum, tin, and potassium sulphoplatinite. When the residue is treated with water in the

absence of air, the soln. contains potassium sulphoplatinite and potassium hydroxide, whilst the undissolved residue is a mixture of platinum, tin, and **potassium hydrosulphoplatinite,** $K_2PtS_2.2H_2PtS_2$. When the soln. is exposed to the air, the potassium sulphoplatinite is partially oxidized according to the equation $3K_2PtS_2+3O=K_2PtO_3+2K_2PtS_3$, and when this oxidized solution is treated with hydrochloric acid, platinic sulphide is precipitated. When potassium sulphoplatinite is treated with dil. hydrochloric acid in absence of air, **sulphoplatinous acid,** H_2PtS_2, is formed which, in the presence of air, is oxidized to water and platinic sulphide. By fusing a mixture of platinous oxystannate, $Pt_2Sn_6O_{10}$, with twice its weight of sulphur, and washing the product, there remains a black powder consisting of acicular crystals of **platinous sulphostannate,** $4PtS.SnS_2$, which is not attacked by boiling nitric or hydrochloric acid, but is decomposed by boiling aqua regia. The salt is stable in air, but when heated, it is completely decomposed into platinum and platinous stannate. R. Schneider observed that when $2Na_2S.2PtS.PtS_2$ is decomposed by boiling water, **sodium sulphoplatinite,** $Na_2S.PtS$, is formed; and he obtained **sodium hydrosulphoplatinite,** $2H_2S.Na_2S.3PtS$, or $Na_2PtS_2.2H_2PtS$, from the red liquid obtained in the preparation of $Na_2S.PtS.2PtS_2$ with absolute alcohol, and washing the precipitate with dil. alcohol (2 : 1), and finally with alcohol. The brown product is converted into platinic sulphide and sodium carbonate on exposure to air. It forms a brown soln. with water from which alcohol precipitates the original salt; and when treated with hydrochloric acid, the sodium is extracted: $2H_2PtS_2.Na_2PtS_2+2HCl=2NaCl+3H_2PtS_2$.

The analyses of the products obtained by L. N. Vauquelin—*vide supra*—approximate to Pt_5S_6, and R. Schneider considers that this salt is actually produced. He considers it to be **platinous tetritasulphoplatinate,** $(PtS)_4PtS_2$, or $Pt_4(PtS_6)$, **platinous hexasulphoplatinate,** and said that it is best prepared by fusing together for 8 to 10 minutes, at a bright red heat, a mixture of 2 parts of ammonium chloroplatinate, and 3 parts each of sulphur, and dry sodium carbonate. It forms steel-grey needles, having a metallic aspect and belonging to the rhombic system. It is unchanged in the air when dry, but if the moist substance be heated on the water-bath it absorbs oxygen, and then contains sulphuric acid. Heated in carbon dioxide it loses one-sixth of its sulphur, platinous sulphide remaining; heated in the air, the sulphur is entirely burned away. When strongly heated in a stream of hydrogen it is entirely reduced. It is unacted upon by boiling hydrochloric or nitric acid, but is slowly attacked by boiling aqua regia. Fused with nitre, it is easily and completely decomposed. R. Schneider prepared **platinous dihydrohexasulphoplatinate,** $Pt_3H_2(PtS_6)$, by the action of warm hydrochloric acid on $K_2S.3PtS.PtS_2$; it readily oxidizes in air to form water and platinum sesquisulphide; if the sodium salt $2Na_2S.2PtS.PtS_2$ be similarly treated in the cold, reddish-brown **platinous tetrahydrohexasulphide,** $Pt_2H_4(PtS_6)$, is formed.

R. Schneider prepared **potassium triplatinous hexasulphoplatinate,** $K_2Pt_3(PtS_6)$, by melting at a high temp. an intimate mixture of 1 to 2 parts of spongy platinum with 6 parts each of sulphur and potassium carbonate. The bluish-grey plates of the salt can be separated by levigation, washed, and dried at 120°. The sp. gr. is 6·44 at 15°. The salt is stable in air at ordinary temp., but when heated, it glows like tinder giving off sulphurous oxides, and forming potassium sulphate and platinum. It is attacked when heated in hydrogen chloride forming hydrogen sulphide; dil. hydrochloric acid forms platinous dihydrohexasulphoplatinate; when heated in hydrogen, hydrogen sulphide is formed. R. Schneider prepared **sodium diplatinous hexasulphoplatinate,** $Pt_2Na_4(PtS_6)$, by melting together a mixture of 1 part of platinum sponge with 6 to 9 parts each of dry sodium carbonate and sulphur, and washing the product with water. The pale copper-red, rhombic needles are coloured brown and black by exposure to air, or aerated water; they are decomposed by boiling water; and sodium sulphide reacts: $Na_2S+PtS+2H_2O=H_2PtS_2+2NaOH$. Dil. hydrochloric acid reacts as indicated

above forming platinous tetrahydrohexasulphoplatinate. The fresh precipitate, in contact with neutral silver, zinc, cadmium, thallous, ferrous, and manganese salts, exchanges sodium for the corresponding metal, but not so with salts of the alkaline earths.

R. Schneider observed that if freshly-prepared sodium diplatinous hexasulphoplatinate is treated with a dil. soln. of copper sulphate, with exclusion of air, there is formed **copper diplatinous hexasulphoplatinate,** $Pt_2Cu_2(PtS_6)$, in bluish-grey pseudomorphs of the sodium salt. The copper salt is stable in air; it glows like tinder when heated leaving a residue of platinum and of copper oxide. Boiling nitric or hydrochloric acid extracts the copper; and the salt is partially decomposed by boiling aqua regia. R. Schneider obtained **silver diplatinous hexasulphoplatinate,** $Pt_2Ag_4(PtS_6)$, by the action of a soln. of silver nitrate on the corresponding sodium salt. If heated in air or in hydrogen, a mixture of silver and platinum is formed. Hydrochloric acid has no perceptible action; warm nitric acid extracts the silver; and hot aqua regia dissolves some platinum and leaves a residue of silver chloride and platinic sulphide. R. Schneider prepared **zinc diplatinous hexasulphoplatinate,** $Pt_2Zn_2(PtS_6)$, **cadmium diplatinous hexasulphoplatinate,** $Pt_2Cd_2(PtS_6)$; **thallous platinic hexasulphoplatinate,** $PtTl_4(PtS_6)$; **stannic diplatinous hexasulphoplatinate,** $Pt_2Sn(PtS_6)$; **lead diplatinous hexasulphoplatinate;** $Pt_2Pb_2(PtS_6)$; **manganese diplatinous hexasulphoplatinate,** $Pt_2Mn_2(PtS_6)$; and **ferrous diplatinous hexasulphoplatinate,** $Pt_2Fe_2(PtS_6)$.

R. Schneider[2] prepared **platinum hemitrisulphide,** or *platinum sesquisulphide,* Pt_2S_3, which he considered to be **platinous sulphoplatinate,** $PtS.PtS_2$, or $Pt(PtS_3)$, platinous trisulphoplatinate, by the spontaneous oxidation of $H_2S.3PtS.PtS_2$; or by the action of a dil. soln. of sodium chloroplatinate on sodium platinosic sulphide, $2Na_2S.2PtS.PtS_2$. The steel-grey powder has a sp. gr. of 5·52. When moist, the powder absorbs oxygen from the air. It loses about 5 per cent. of water at 120°; and at a higher temp. it suddenly swells up and gives off more water; at a still higher temp., sulphur is sublimed. When roasted in air, it begins to glow like tinder giving off sulphurous oxides, and finally leaving a residue of platinum sponge. It is easily reduced in hydrogen; it is not attacked by boiling nitric or hydrochloric acid; but it is slowly attacked by boiling aqua regia. If $Na_2S.PtS.2PtS_2$ be suspended in water and treated with dil. hydrochloric acid, there is formed unstable **platinous hydrotrisulphoplatinate,** $PtH_2(PtS_3)_2$, or $PtS.H_2S.2PtS_2$, which is readily decomposed on exposure to air, forming platinic sulphide. R. Schneider observed that **sodium platinous trisulphoplatinate,** $PtNa_2(PtS_3)_2$, or $PtS.Na_2S.2PtS_2$, is formed when sodium diplatinous hexasulphoplatinate is boiled with water. The brown, crystalline powder rapidly darkens on exposure to air, and water, sodium carbonate, and platinic sulphide are formed; with dil. hydrochloric acid, platinous hydrotrisulphoplatinate is formed.

The mineral cooperite was at first represented by $Pt(As, S)_2$, then by PtS_2, and later by PtS (*q.v.*). E. Davy prepared **platinic sulphide,** or **platinum disulphide,** PtS_2, by heating to low redness a mixture of 2 parts of sulphur with 3 parts of ammonium chloroplatinate in a glass tube closed with mercury, and stopping the heating when the evolution of gas has ceased. R. Böttger said that the product is contaminated with sulphur because the mixture has not been heated long enough. W. Biltz and R. Juza, and H. G. Krall also prepared the disulphide from its components, and by heating sulphur with platinic chloride. E. A. Geitner heated hydrochloroplatinic acid decolourized by sulphur dioxide, to 200° in sealed tubes. J. Persoz heated to whiteness a mixture of platinum with 2 parts of sodium carbonate and 3 parts of sulphur, and washed the product with water; the platinic sulphide remains in long, aurora-red needles. L. Wöhler and co-workers obtained it by the action of hydrogen sulphide on platinic chloride, and by heating the product with sulphur at 600°. R. Böttger prepared the sulphide by allowing a mixture of 1 part of dry platinic chloride, 4 parts of absolute alcohol, and 5 parts of carbon disulphide to stand in a stoppered bottle for a week with occasional shaking. The

product is then washed with 80 per cent. alcohol to remove the carbon disulphide, rubbed to a pasty mass, and boiled with a large proportion of water. The product is then washed with water until free from chlorides; pressed between bibulous paper; and dried in vacuo over sulphuric acid at a temp. below 125°. J. J. Berzelius treated a platinic salt with hydrogen sulphide, or an alkali sulphide, washed the precipitate with boiling water, and dried it in vacuo; U. Antony and A. Lucchesi, passed hydrogen sulphide through a 3 per cent. soln. of hydrochloroplatinic acid at 90°—if the temp. is below 90°, sulphoplatinates are formed—washed the product in an atm. of hydrogen sulphide and dried it at 70° to 80° until the weight was constant. R. Schneider obtained platinic sulphide by exposing moist sodium diplatinous hexasulphoplatinate or platinous tetrahydrohexasulphoplatinate to atm. air as indicated above.

Platinic sulphide is a dark brown, steel-grey, or black powder. L. Thomassen found that the X-radiogram corresponds with a trigonal lattice having a=3·537 A., c=5·019 A., and $a:c$=1 : 1·419. F. A. Bannister gave a=3·54 A., and c=5·02 A. The sp. gr., according to E. Davy, is 3·5. R. Schneider found this datum is too low, and gave 5·27 for the sp. gr. This is still too low for F. A. Bannister gave 7·86; and W. Biltz and R. Juza gave 7·66, and 33·9 for the mol. vol. E. Davy said that the sulphide does not fuse when heated. R. Böttger found that the thermal decomposition begins between 225° and 250°, and, according to J. J. Berzelius, an atom of sulphur is first given off and platinous sulphide is formed. W. Biltz and R. Juza measured the vap. press. of the sulphur and obtained the isothermal curves indicated in Fig. 94. The heat of formation of the disulphide from the solid monosulphide and solid rhombic sulphur is 5 Cals. Only the di- and monosulphides were observed. According to R. Schneider, when the disulphide is heated in air, it glows like tinder, leaving behind spongy platinum. E. Davy said that the disulphide is a non-conductor of electricity. W. Skey discussed the behaviour of the disulphide as a cathode in electrolyses. R. Böttger said that the sulphide is not decomposed by hydrogen at ordinary temp. E. Pollacci said that platinic sulphide readily oxidizes in air; E. Davy also observed that some preparations are not decomposed by air or water at ordinary temp., and P. de Clermont and J. Frommel added that boiling water has no action; but J. J. Berzelius' preparation when moist was observed to produce sulphuric-acid on exposure to air, and to char paper on which it rested. J. J. Berzelius' preparation is much more sensitive to chemical reagents than is the case with the other preparations. L. R. von Fellenberg showed that at a dull red-heat, chlorine decomposes platinic sulphide producing platinum and sulphur chloride. R. Böttger observed that boiling conc. sulphuric, hydrochloric or nitric acid of sp. gr. 1·2 has no action on the sulphide; and E. Davy, and R. Schneider added that of all the acids tried, hot aqua regia alone exerts a slight action on this compound. J. J. Berzelius' preparation was observed to be rapidly decomposed by aqua regia, and to be slowly and completely dissolved by fuming nitric acid. A. Guerout found that sulphurous acid has no perceptible action on the compound.

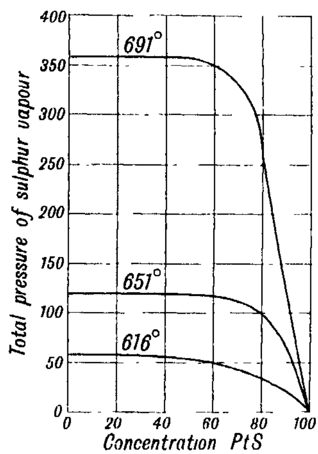

Fig. 94.—The Isothermal Dissociation of Platinum Disulphide.

According to J. J. Berzelius, when hydrogen sulphide is passed over precipitated, black platinic sulphide, the compound acquires a reddish-brown colour by absorption of gas, but on exposure to air, the gas is given off and the black colour is restored. E. von Meyer also indicated that the pale brown precipitate obtained by hydrogen sulphide with hot soln. of potassium chloroplatinate is *eine*

lockere Verbindung of platinic and hydrogen sulphides, which loses its hydrogen sulphide when washed with hot water. K. A. Hofmann and F. Höchtlen obtained dark brown **platinic dihydrotrisulphide,** $PtS_2.H_2S$, or $PtS(HS)_2$, or H_2PtS_3, by the action of dry hydrogen sulphide on a soln. of platinic chloride in absolute alcohol, and washing the product with carbon disulphide to remove free sulphur. U. Antony and A. Lucchesi obtained **platinic hydrosulphide,** $Pt(HS)_4$, or $PtS_2.2H_2S$, by the first action of hydrogen sulphide on a dil. soln. of hydrochloroplatinic acid at ordinary temp., the continued passage of the gas produces some decomposition. P. Schützenberger prepared **platinic thiocarbide,** S : Pt : C : Pt : S.

R. Böttger observed that boiling aq. ammonia, and ammonium sulphide have no perceptible action on the sulphide. J. Ribau observed that the sulphide is insoluble in ammonium or alkali sulphides or polysulphides; and P. de Clermont, that it is insoluble in boiling soln. of ammonium salts. J. J. Berzelius' preparation dissolves completely in aq. soln. of alkali sulphides or hydroxides forming platinum and alkali thiosulphates. R. Böttger observed that platinic sulphide is decomposed when it is kneaded with potassium at ordinary temp., and intense combustion occurs; sodium does not act until it is warmed. Boiling soln. of potassium hydroxide, or sodium carbonate do not act on the sulphide. E. Davy said that the sulphide is decomposed when heated with zinc, or when fused with potassium chlorate, or hydroxide, and, added R. Böttger, with potassium nitrate. W. Skey observed that platinum disulphide reduces auric chloride.

C. Winssinger obtained a **colloidal solution** of platinic sulphide by dialyzing the liquid obtained by the action of hydrogen sulphide on a very dil. soln. of a platinic salt. U. Antony and A. Lucchesi employed a 3 per cent. soln. of hydrochloroplatinic acid, or sodium chloroplatinate at 15° to 18°. G. Hofmeier employed 50 c.c. of a 1 : 1,000 aq. soln. of platinic chloride, diluted it to 200 c.c. and passed the gas for a short time at 50° to 60°, and dialyzed the liquid. J. C. H. Heyer, and T. Svedberg added yellow soln. of ammonium sulphide to a soln. of platinic chloride. G. Hofmeier recommended gum arabic as a protective colloid. The colloidal soln. is brown or brownish red in transmitted light, and dark grey in reflected light. The colloidal sulphide is coagulated by heat, by evaporation, by hydrochloric acid, alkali chlorides, barium sulphate, and animal charcoal.

According to J. J. Berzelius, platinic sulphide precipitated by hydrogen sulphide dissolves in ammonium sulphide to form a reddish-brown soln. of what was thought to be **ammonium sulphoplatinate,** $(NH_4)_2PtS_3$. The liquid—possibly a colloidal soln.—deposits platinic sulphide when treated with acids. K. A. Hofmann and F. Höchtlen prepared **ammonium polysulphoplatinate,** $(NH_4)_2PtS_3.S_{12}.2H_2O$, by saturating a 25 per cent. soln. of ammonium sulphide with sulphur at 30°, and dropping the liquid, with constant stirring, into a cold, 10 per cent. soln. of platinic chloride. The reddish-brown precipitate is allowed to stand in a closed vessel for 2 or 3 days at 5°, filtered by suction, washed with carbon disulphide, and dried some hours in vacuo over sulphuric acid. The red, rhombic pyramids are stable when dry; they are insoluble in ether; and form a yellowish-red soln. with alcohol. J. J. Berzelius obtained a green mass—possibly **potassium sulphoplatinate,** K_2PtS_3, when potassium disulphide is fused in a platinum crucible. The aq. soln. deposits platinic sulphide. Precipitated platinic sulphide is soluble in aq. soln. of potassium sulphide; and similarly also with sodium sulphide, and as indicated above, it is possible that the soln. contains **sodium sulphoplatinate,** Na_2PtS_3. The preparation of L. N. Vauquelin, and J. Persoz, indicated above in connection with platinic sulphide, may have contained sodium sulphoplatinate.

F. W. Semmler prepared **platinic disulphovinylsulphine,** $[Pt\{(C_2H_3)_2S\}S_2]$, and **platinic disulphovinylsulphinechloroplatinite,** $[Pt\{C_2H_3)_2S\}S_2].2(C_2H_3Cl)PtCl_4$; T. Wertheim, **platinic disulphoallylsulphine,** $[Pt\{(C_3H_5)_2S\}S_2]$;—*vide* the sulphine salts of the halides, etc.

According to J. J. Berzelius, moist, precipitated platinic sulphide when exposed to air forms sulphuric acid, and in many respects behaves like J. W. Döbereiner's

platinum black. The precipitated sulphide, indeed, contains some free platinum. R. Böttger observed that if the precipitated sulphide be exposed to air, with constant stirring, at 50° to 62°, it forms a black powder, which when heated to 100° in a retort becomes violet-black. It is supposed to contain some *oxidized platinic sulphide*. Its sp. gr. is 6·286 ; it has a sour taste ; forms sulphuric acid when treated with water ; takes fire in air at 250°, burning with a hissing noise and violet flame, with the evolution of sulphurous oxides ; and it becomes warm in a current of hydrogen above 25° and decrepitates giving off hydrogen sulphide, and leaving a residue of spongy platinum.

E. von Meyer doubted if the so-called "oxidized sulphide" contains **platinic oxysulphide,** PtOS, but it may contain the normal platinum **dihydroxysulphide,** $Pt(OH)_2S$, or else $(PtS)_2O(OH)_2$. The former is said to be the first stage in the oxidation of platinic sulphide; and the **platinic oxydihydroxydisulphide,** $(PtS)_2O(OH)_2$, or $PtOS.\frac{1}{2}H_2O$, is produced when the dark brown precipitate formed by hydrogen sulphide in hot soln. of potassium chloroplatinate, or nearly neutral soln. of platinic chloride, and washing free from chlorides, is dried on a water-bath, and heated, with frequent stirring, for about 10 days at 70° to 100°. The product is washed with hot water, and the treatment repeated. The product is finally dried at 100° to 110° in a current of carbon dioxide. If the temp. of desiccation is higher than this, oxidation occurs. When the powder is warmed in air, sulphurous oxides are evolved, and platinum is formed. Hydrogen forms platinous sulphide and water ; nascent hydrogen slowly forms hydrogen sulphide ; chlorine in the presence of moisture forms sulphuric and hydrochloric acids ; conc. hydrochloric acid reacts slowly without the evolution of chlorine, and after some time the soln. contains a little sulphuric acid ; hydrogen sulphide forms water and sulphur ; sulphur dioxide forms sulphur trioxide with the evolution of heat ; sulphurous acid is slowly oxidized ; ammonia is rapidly absorbed with the evolution of heat and the formation of water ; nitrous and nitric oxides do not react with the oxysulphide ; carbon monoxide forms platinous sulphide and carbon dioxide ; oxalic acid slowly decomposes with the evolution of carbon dioxide ; methyl alcohol is oxidized to formaldehyde ; ethyl alcohol becomes warm and forms aldehyde and acetic acid ; toluene is partially converted into benzaldehyde ; potassium permanganate is slowly reduced ; and ferrous salts are slowly converted into ferric salts.

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§ 28. Platinous Sulphates

P. T. Cleve [1] obtained the ammine of *platinum subsulphate*, Pt_2SO_4 or *platinum hemisulphate*, namely, **platinum tetramminosulphate,** $Pt_2(NH_3)_4SO_4$, as a black, amorphous powder, by the action of dil. sulphuric acid on the corresponding hydroxide. According to J. J. Berzelius, **platinous sulphate,** $PtSO_4$, is known only in aq. soln., not in the crystalline state. Hydrated platinous oxide dissolves in dil. sulphuric acid forming a dark brown soln. which assumes a redder tint when diluted with water, and becomes darker on exposure owing to oxidation. L. N. Vauquelin observed that when sulphuric acid is heated with platinous chloride until all the chlorine is expelled, and evaporated, a black, amorphous mass is produced which deliquesces in air, and a conc. aq. soln. is black and yellowish-green when dilute. The soln. loses its colour in a few days with the deposition of hydrated platinous oxide. A. Litton and G. H. E. Schnedermann also observed that the brown soln. of platinous sulphate deposits platinum when diluted sufficiently.

J. Reiset prepared **platinous tetramminosulphate,** $[Pt(NH_3)_4]SO_4$, by evaporating the liquid obtained when the corresponding chloride is treated with silver sulphate; and M. Peyrone, P. T. Cleve, and H. and A. Euler, by mixing platinous diamminodichloride with sulphuric acid, dissolving the precipitate in hot water, neutralizing with ammonia, and cooling the liquid. The salt can be recrystallized from aq. soln. C. Weltzien also described this salt. H. Töpsöe observed that the colourless, tetragonal crystals have the axial ratio $a:c=1:1{\cdot}8278$; the (001)-cleavage is complete, and the (111)-cleavage incomplete. The optical character is negative. Observations on the crystals were also made by A. E. Nordenskjöld, and Q. Sella. E. Rosenbohm studied the magnetic susceptibility. J. Lang observed that the salt does not decompose at 220°, and J. Reiset, that decomposition begins at 270°. A. A. Grinberg and B. V. Ptitsin studied the thermal decomposition of the salt. The salt is more soluble in hot than it is in cold water; 100 parts of water at 16·5° dissolve 3·125 parts of salt, M. Peyrone's value is less than this. The aq. soln. is neutral. P. T. Cleve found that with bromine, the dibromotetramminosulphate is formed. M. Peyrone, and P. T. Cleve observed that with sulphuric acid, **platinous tetramminohydrosulphate,** $5[Pt(NH_3)_4]SO_4.4H_2SO_4.4H_2O$, is formed; and H. and A. Euler, and P. T. Cleve also prepared $3[Pt(NH_3)_4]SO_4.H_2SO_4.H_2O$. M. Peyrone observed that nitric acid forms a blue soln. with the

tetramminosulphate, and when the liquid is boiled, and the product dissolved in water, $[Pt(NH_3)_4(OH)(NO_3)](NO_3)_2$, is formed. The tetramminosulphate is insoluble in alcohol. P. T. Cleve reported platinous triamminosulphate, $Pt(NH_3)_3SO_4$, to be formed by treating the corresponding chloroplatinite with silver sulphate, evaporating the filtrate, and drying the snow-white mass of crystals at 100°. E. Rosenbohm studied the magnetic susceptibility. The salt is sparingly soluble in cold water, but readily soluble in hot water. L. A. Tschugaeff and I. Tscherniaeff prepared **platinous octammino-diol-sulphate,** $[(NH_3)_4Pt{\cdots}(OH)_2{\cdots}Pt(NH_3)_4]SO_4$, as indicated in connection with the aquotriammines. R. Uhlenhuth prepared triclinic crystals of **platinous tetrahydroxylaminosulphate,** $Pt(NH_2OH)_4SO_4$. L. A. Tschugaeff and M. S. Grigorieff prepared **platinous tetrahydrazinosulphate,** $[Pt(N_2H_4)_4]SO_4$.

J. Reiset, P. T. Cleve, and L. Ramberg prepared **platinous trans-sulphatodiammine,** $[Pt(NH_3)_2(SO_4)].H_2O$, by boiling the corresponding iodide or the chloride with silver sulphate, and evaporating the clear liquor. The air-dried salt does not lose water at 120°, but at higher temp. water is lost in the decomposition. The salt is sparingly soluble in cold water, but more soluble in hot water. The aq. soln. reacts acidic. Soluble chlorides precipitate from the aq. soln. the dichlorodiammine ; aqua regia forms platinic *trans*-tetrachlorodiammine ; iodine tincture forms platinic tetraiododiammine ; and aq. ammonia forms platinous tetramminosulphate. P. T. Cleve obtained the corresponding **platinous cis-sulphatodiammine,** from the corresponding cis-dichlorodiammine.

C. Enebuske described **platinous quatermethylaminesulphinosulphate,** $[Pt\{(CH_3)_4S\}SO_4]$; A. Wurtz, and H. Wolfram, **platinous quaterethylaminesulphate,** $[Pt(C_2H_5NH_2)_4]SO_4$; P. T. Cleve, **platinous transbisethylaminediamminosulphate,** $[Pt(NH_3)_2(C_2H_5NH_2)_2]SO_4$, as well as the *hexahydrate*; P. T. Cleve, **platinous bisanilinediamminosulphate,** $[Pt(NH_3)_2(C_6H_5NH_2)_2]SO_4$; A. Werner, **platinous bispropylenediaminesulphate,** $[Pt\{C_3H_6(NH_2)_2\}_2]SO_4$; S. G. Hedin, **platinous trans-sulphatobispyridine,** $[Pt(C_5H_5N)_2SO_4].2H_2O$ and **platinous cis-sulphatobispyridine**; also **platinous hydroxysulphatobispyridine,** $[Pt(C_5H_5N)_2(OH)(SO_4)(OH)Pt(C_5H_5N)_2]$; **platinous quaterpyridinesulphate,** $[Pt(C_5H_5N)_4]SO_4$, **platinous quaterpyridinehydrosulphate,** $[Pt(C_5H_5N)_4](HSO_4)_2$, alone and associated with pyridine ; there are also the double sulphates **platinous quaterpyridinesulphatocuprate,** $[Pt(C_5H_5N)_4]Cu(SO_4)_2.8H_2O$, and **platinous quaterpyridinesulphatozincate,** $[Pt(C_5H_5N)_4]Zn(SO_4)_2.12H_2O$. A. Rosenheim and W. Handler prepared **platinous bis-m-tolylenediamine,** $[Pt(C_7H_{10}N_2)_2]SO_4.3H_2O$.

C. Enebuske described **platinous sulphatobismethylsulphine,** $[Pt\{(CH_3)_2S\}_2SO_4].2H_2O$; C. W. Blomstrand, **platinous sulphatobisethylsulphine,** $[Pt\{(C_2H_5)_2S\}_2SO_4].7H_2O$; H. Londahl, **platinous trisethylsulphinesulphate,** $Pt\{(C_2H_5)_2S\}_3SO_4.4H_2O$; and **platinous tris-i-butylsulphinesulphate,** $Pt\{(C_4H_9)_2S\}_3SO_4$; C. Rudelius, **platinous sulphatobispropylsulphine,** $[Pt\{(C_3H_7)_2S\}_2SO_4]$, with normal and iso-propyl ; H. Löndahl, **platinous sulphatobisbutylsulphine,** $[Pt\{(C_4H_9)_2S\}_2SO_4]$, **platinous sulphatodibenzylsulphine,** $[Pt\{(C_6H_5CH_2)_2S\}_2SO_4]$, **platinous bisethylenesulphinesulphate,** $[Pt\{(C_2H_4)_2S_2\}_2]SO_4$, **platinous ethylenesulphineamminosulphate,** $[Pt\{(C_2H_4)_2S_2\}(NH_3)]SO_4$; **platinous ethylenesulphinetriamminosulphate,** $[Pt(NH_3)_3\{(C_2H_4)_2S_2\}]SO_4$; and **platinous sulphatoethylenesulphine,** $[Pt\{(C_2H_4)_2S_2\}SO_4]$; P. T. Cleve, **platinous trisanilinediamminosulphate,** $[Pt(NH_3)_2(C_6H_5NH_2)_3]SO_4$; L. Ramberg, **bisethylthioglycolatodiamminosulphate,** $[Pt(NH_3)_2(H.CO_2CH_2.S.C_2H_5)_2]SO_4$; N. S. Kurnakoff, **platinous quaterthioacetamide,** $[Pt(CH_3.CS.NH_2)_4]SO_4$; N. S. Kurnakoff, and W. J. Sell and T. H. Easterfield, **platinous quaterthiocarbamidesulphate,** $[Pt\{CS(NH_2)_2\}_4]SO_4$; K. A. Jensen, **platinous thiocarbazidosulphate,** $[Pt(thio)_2]SO_4$. N. S. Kurnakoff, **platinous quaterxanthogenamidesulphate,** $[Pt(NH_2.CS.OC_2H_5)_4]SO_4$; R. Bunsen, **platinous sulphatoxycacodyl,** $[Pt\{As_2(CH_3)_4O\}SO_4]$; L. Ramberg, **platinous trans-sulphatodiamminobisethylthiolglycolate,** $Pt(NH_3)_2(CO_2H.CH_2.S.C_2H_5)_2.H_2O$. J. Petren, **platinous quaterethylselenine,** $[Pt\{(C_2H_5)_2Se\}_4]SO_4$; **platinous sulphatobisethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2SO_4]$, **platinous sulphatotrisethylselenine,** $[Pt\{(C_2H_5)_2Se\}_3SO_4.4H_2O$, **platinous sulphatoethylsulphinepyridine,** $[Pt(C_5H_5N)\{(C_2H_5)_2Se\}SO_4]$, and **platinous sulphatoethylsulphinoethylselenine,** $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}SO_4]$.

L. N. Vauquelin obtained a dark green precipitate by evaporating a mixed soln. of platinous and potassium sulphates. The dried mass is black and probably represents an impure **potassium sulphatoplatinite.** At a red heat, it leaves a residue of platinum and potassium sulphate.

E. Prost reported a subsulphide, **ammonium subsulphatoplatinite,** $2(NH_4)_2SO_4.Pt_8(SO_4)_2.25H_2O$, to be formed by adding alcohol to a mixed soln. of ammonium and platinum subsulphate.

Some sulphates of what is regarded as tervalent platinum have been investigated. They are here called the platinosic sulphates. M. Delépine reported that a **platinosic dihydroxyhydrosulphate,** $Pt(OH)_2(HSO_4).H_2O$, can be obtained by boiling platinum with sulphuric acid for a long time when the liquid gradually darkens in colour until finally, after 30 hrs., it becomes almost black when it contains about 20 grms. of platinum per litre. The soln. can be diluted with water, or it can be evaporated to dryness, the residue taken up with water, and when the soln. is treated with half its vol. of conc. sulphuric acid, it furnishes black plates. Since at 100° this compound loses 1·5 mols. of water per atom of platinum, it might be represented by the formula $O\{Pt(OH)(HSO_4)\}_2.3H_2O$; and since it can be converted into an equimolar mixture of H_2PtCl_4 and H_2PtCl_6, it was inferred that the platinum in the compound is tervalent. The compound crystallizes from aq. soln. in black, rectangular prisms. The compound is extremely soluble in water, conc. sulphuric acid, acetic acid, alcohol, and acetone forming reddish-brown soln. with ether it forms a compound containing 2 mols. of ether, which is insoluble in ether. Alkali lye precipitates from the soln. a dark brown oxide.

According to M. Blondel, **platinosic hydroxydihydrosulphate,** $Pt(OH)(HSO_4)_2.9\frac{1}{2}H_2O$, can be represented as $Pt_2(OH)_6(SO_3)_4(OH)_2.8\frac{1}{2}H_2O$, and L. Wöhler and W. Frey consider it to be a hydrosulphatoplatinosic acid analogous to hydrochloroplatinic acid. M. Blondel, and M. Delépine showed that when platinum dissolves in boiling sulphuric acid in an atm. of carbon dioxide, the reaction $2Pt+7H_2SO_4 \rightleftharpoons 3SO_2+4H_2O+2(HO)Pt(HSO_4)_2$, is reversible ; when air was used, twice as much platinum dissolved, and less sulphur dioxide was evolved, owing to the oxidation of the sulphur dioxide to trioxide under the influence of the platinum. With oxygen, four times as much platinum dissolved, and less still sulphur dioxide was evolved. When a mixture of carbon and sulphur dioxides was used, no soln. of platinum took place, and, in some cases, platinum was precipitated from soln. M. Blondel observed that in J. J. Berzelius' process for preparing platinic sulphate, this compound is in part obtained because platinic oxide is slowly reduced to platinosic oxide at about 110°. E. Prost reported that $Pt_8O_{13}SO_4.16H_2O$ is precipitated when a soln. of platinic sulphate, free from nitric acid, is boiled. M. Blondel prepared this compound by reducing a soln. of platinic sulphate in sulphuric acid by means of oxalic acid, and L. Wöhler and W. Frey employed the same reducing agent. The orange-red prisms or plates were found by M. Blondel to be triclinic pinacoids with the axial ratios $a:b:c=1\cdot6236:1:0\cdot5492$, and $\alpha=90° 29'$, $\beta=101° 53'$, and $\gamma=88° 55'$; the (010)-cleavage is complete. The salt effloresces in dry air, and when dried over sulphuric acid under reduced press., it forms the stable $Pt(OH)(HSO_4)_2$. This compound does not change at 110°, but at 150° it begins to lose sulphur trioxide, and is partially reduced. When exposed to moist air for some days it forms a gum-like mass. The aq. soln. decomposes slowly in the cold, and more quickly when heated, forming a brown precipitate with a variable composition. An excess of hydrochloric acid produces a mixture of platinous and platinic chlorides. The acid is dibasic. Although the addition of the eq. of 2 mols. of sodium hydroxide forms a crystallizable sodium salt, more alkali can be added because the salt is gradually polymerized with the liberation of acid in a colloidal form. When an excess of the alkali lye is added to a boiling soln., a polymerized form of platinum sesquioxide is precipitated. Sodium, potassium, and barium hydroxides and the oxides of thallium, iron, and silver form crystallizable salts. Aq. soln. of the acid give no precipitate at first with barium chloride, but they do so after standing some time. This acid therefore has some analogies with the complex sulphates of iron and chromium studied by A. Recoura. L. Wöhler and W. Frey found that the titration with a soln. of potassium permanganate agrees with the assumption that the compound contains tervalent platinum.

The platinic dihydroxyhexammino-μ-aminodisulphate, $[(OH)(NH_3)_3Pt(NH_2)Pt(NH_3)_3(OH)](SO_4)_2$ of P. T. Cleve, obtained in snow-white needles by the action of dil. sulphuric acid on the corresponding nitrate, has been regarded as **platinosic**

hydroxytetramminosulphate, $Pt(OH)(SO_4).4NH_3.H_2O$. M. Delépine prepared **potassium platinosic sulphate** $K_2SO_4.Pt_2(SO_4)_3.2H_2O$, or $KPt(SO_4)_2.H_2O$, by adding potassium sulphate to a soln. of platinum in sulphuric acid ; and M. Blondel, by adding a potassium salt to a soln. of platinosic hydroxydihydrosulphate. The straw-yellow needles or prisms are stable at 150°. The salt is sparingly soluble in water ; it is decomposed by boiling water ; and, in time, in cold water, impure hydrated platinosic oxide is precipitated. It is vigorously reduced by alcohol. M. Blondel obtained orange-red prisms of **sodium platinosic sulphate,** $Na_2SO_4.Pt_2(SO_4)_3.8H_2O$, or $NaPt(SO_4)_2.4H_2O$, in a similar manner. The monoclinic prisms have the axial ratios $a:b:c=1\cdot1127:1:0\cdot6898$, and $\beta=94°\ 31'$. The crystals do not effloresce in dry air ; at 100° water is slowly given off and an uncrystallizable product is formed. The salt is freely soluble in water. M. Blondel also obtained crystalline **silver platinosic sulphate,** $Ag_2SO_4.Pt_2(SO_4)_3.nH_2O$; **barium platinosic sulphate,** $BaSO_4.Pt_2(SO_4)_3.nH_2O$; **thallous platinosic sulphate,** $Tl_2SO_4.Pt_2(SO_4)_3.nH_2O$; and **ferrous platinosic sulphate,** $FeSO_4.Pt_2(SO_4)_3.nH_2O$. M. Blondel's compounds, together with the **sulphatoplatinosic acid,** $HPt(SO_4)_2.6H_2O$, are considered by H. D. K. Drew and H. J. Tress to be salts of tervalent platinum.

D. Schou prepared **platinous dichlorodiamminochlorocarbonate,** $2[Pt(NH_3)_2Cl_2]$-$[\{Pt(NH_3)_2Cl_2\}_2(CO_3)]$, by mixing a soln. of potassm chloroplatinite in water at 40° with a mixture of ammonium hydrocarbonate and water, and then passing carbon dioxide through the soln. until it acquires an indigo-blue colour and some quantity of a blackish-blue precipitate is deposited. The soln. is precipitated with alcohol, and the precipitate washed successively with water and alcohol, and dried by exposure to the air. It forms small crystals and aggregates, is sparingly soluble in water, insoluble in alcohol and ether, is gradually decomposed by cold hydrochloric acid, and, by boiling with the acid, is converted into platinous dichlorodiammine. When boiled with ammonia, a small quantity remains undissolved, and the soln. when saturated with hydrogen chloride and treated with potassium chloroplatinite gives a precipitate of Magnus' green salt, $[Pt(NH_3)_4]$-$PtCl_4$. When treated with a slight excess of silver nitrate, a yellow soln. of platinous dinitratodiammine is obtained.

N. W. Fischer, and A. von Mussin-Puschkin observed that **platinic sulphate,** $Pt(SO_4)_2$, is formed when platinum is boiled in sulphuric acid ; J. J. Berzelius, that soln. of hydrated platinic oxide or of platinic chloride in sulphuric acid furnish this sulphate on evaporation ; and E. Davy that the repeated evaporation to dryness of fuming nitric acid and platinic sulphide furnishes this salt. It was said that the black porous mass has a sour, metallic taste, somewhat sharp ; that on ignition at a red heat, it leaves metallic platinum behind ; it deliquesces quickly in air ; it forms a dark brown soln. with water and with hydrochloric, nitric or phosphoric acid, and in alcohol, and ether. J. J. Berzelius said that alkali lye precipitates a basic salt from the aq. soln., and J. von Liebig, that alkali lye does not precipitate platinic oxide from the aq. soln. All this, said M. Blondel, indicates that platinosic hydroxydihydrosulphate was formed ; he also said that normal platinic sulphate does not exist ; and E. Prost added that the chemical individuality of neither the normal sulphate nor double salts of the type $R_2SO_4.Pt(SO_4)_2$, has been established.

According to L. Stuchlik, the soln. of platinum in sulphuric acid of sp. gr. 1·840, obtained by M. Margules, by means of an alternating current, deposits yellow crystals which retain sulphuric acid after several recrystallizations from water. By repeatedly crystallizing the salt from water, in vacuo, large orange leaflets of the *tetrahydrate*, $Pt(SO_4)_2.4H_2O$, are obtained. The salt loses water in a desiccator, and becomes darker in colour. The anhydrous salt exhibits a green metallic lustre. The salt containing sulphuric acid is stable, losing little in weight at 100°, and retaining its orange colour. Both salts dissolve readily in water, the hydrated salt forms a yellow soln., and the anhydrous salt, a dark soln. The yellow soln. deposits a brown basic salt when warmed, sulphuric acid precipitates

the hydrated sulphate from the dark-coloured soln. The sulphuric acid soln. of M. Margules gives brown precipitates when treated with potash or soda lye ; and with aq. ammonia, a pale yellow precipitate is formed.

B. Gerdes prepared **platinic hexamminosulphate,** $[Pt(NH_3)_6](SO_4)_2.H_2O$, by the action of sulphuric acid or of a soluble sulphate on a salt of the hexammine. The white, crystalline powder is almost insoluble in water. L. Tschugaeff and N. Vladimiroff, and W. Palmaer prepared **platinic chloropentamminosulphate,** $[Pt(NH_3)_5Cl]_2(SO_4)_3$; and I. I. Tscherniaeff prepared $[Pt(NH_3)_5(H_2O)](SO_4)_2$, and $Pt(NH_3)_5(OH)(HSO_4)SO_4$. P. T. Cleve prepared **platinic dihydroxytetramminosulphate,** $[Pt(NH_3)_4(OH)_2]SO_4$, by boiling the corresponding hydroxysulphatotetramminosulphate with an equivalent amount of barium hydroxide ; O. Carlgren and P. T. Cleve, and A. Werner, by the action of hydrogen dioxide on a warm soln. of platinous tetramminosulphate, and recrystallizing from hot water; and N. Tarugi, by the action of a conc. ammoniacal soln. of ammonium persulphate on an excess of an aq. soln. of platinic chloride, and warming the mixture to dissolve the ammonium chloroplatinate which is first precipitated, and when the liquid is decolourized the salt separates out. The prismatic crystals do not lose weight over conc. sulphuric acid, or at 100°. The salt is sparingly soluble in boiling water. A. Werner gave for the conductivity, μ, of a soln. with a mol of the salt in 125, 250, 500, and 1000 litres, respectively, 134·38, 162·36, 181·61, and 196·53, in agreement with a 3-ion salt. I. I. Tscherniaeff and S. I. Chorunshenkoff studied the ionization constants. Hydrochloric acid forms the dichlorotetramminochloride ; and barium chloride precipitates all the sulphate. O. Carlgren and P. T. Cleve, and A. Werner obtained the *tetrahydrate*, and O. Carlgren and P. T. Cleve, the *monohydrate*. P. T. Cleve prepared **platinic hydroxysulphatotetramminosulphate,** $[Pt(NH_3)_4(OH)(SO_4)]_2SO_4.3H_2O$, by boiling an aq. soln. of platinic dibromotetramminosulphate with about two molar proportions of silver sulphate until all the bromide is precipitated ; and A. Werner, by boiling an aq. soln. of platinous tetramminosulphate with two molar proportions of bromine added drop by drop. The soln., filtered hot, furnishes tabular crystals on cooling. The salt is sparingly soluble in water. Barium salts precipitate from the soln. only one-third the sulphate; conc. sulphuric acid forms a colourless soln. C. Gerhardt, and C. Weltzien prepared **platinic disulphatodiammine,** $[Pt(NH_3)_2(SO_4)_2]$ by dissolving the hydroxide in sulphuric acid; and P. T. Cleve prepared the *trihydrate*. P. T. Cleve prepared **platinic trans-dihydroxysulphatodiammine,** $[Pt(NH_3)_2(OH)_2(SO_4)].H_2O$, by the action of silver sulphate on the corresponding chloride. The straw-yellow crystalline salt is sparingly soluble in water ; and he also obtained **platinic cis-dihydroxysulphatodiammine.** E. Davy obtained what P. T. Cleve considered to be **platinic sulphatotetramminohydroxide,** $[Pt(NH_3)_4SO_4](OH)_2$, by boiling a soln. of platinic sulphate neutralized with ammonia for a few minutes, and when the soln. is decolourized allowing it to cool. The pale brown powder detonates slightly when heated; it is insoluble in water. A. R. Klien studied the action of water, acids, and alkaline soln. P. T. Cleve obtained **platinic sulphatotetramminosulphate,** $[Pt(NH_3)_4SO_4]SO_4.H_2O$, by the action of conc. sulphuric acid on the hydroxynitratotetramminonitrate. The white salt loses $\frac{2}{3}$ mol. of water at 100°, there is no further loss at 120°, and decomposition occurs at 130°. P. T. Cleve reported **platinic dihydroxyhexammino-μ-diaminesulphate,** $[(OH)(NH_3)_3Pt(NH_2)_2Pt(NH_3)_3(OH)](SO_4)_2$, by the action of sulphuric acid on the corresponding nitrate.

H. Alexander prepared **platinic tetrahydroxylaminesulphate,** $[Pt(NH_2OH)_4](SO_4)_2H_2O$, by digesting the hydroxide, chloride, or oxalate with the theoretical amount of sulphuric acid on a water-bath, filtering the hot liquid, and allowing it to cool. R. Uhlenhuth employed a similar process, and said that the crystals are triclinic prisms. According to H. Alexander, the salt loses about 3·3 per cent. of water at 80° to 90°, and it decomposes at 100° with a slight detonation. It is sparingly soluble in cold water, and readily soluble in hot water with a slight decomposition. The neutral aq. soln. decomposes on a water-bath with the separa-

tion of brown flecks, and of platinum. It can be recrystallized from water, or from dil. sulphuric acid. F. Hoffmann reported **platinic dihydroxylaminediammino-sulphate,** $[Pt(NH_3)_2(NH_2OH)_2](SO_4)_2$, by the action of the corresponding chloride on silver sulphate, or by the action of the theoretical amount of sulphuric acid on the oxalate. The yellow, prismatic crystals are soluble in water at ordinary temp.; the soln. becomes turbid at 30°. P. T. Cleve described **platinic hydroxyacetato-tetramminosulphate,** $[Pt(NH_3)_4(OH)(C_2H_3O_2)]SO_4.1\frac{1}{2}H_2O$. W. J. Pope and S. J. Peachey prepared **trimethyl platinic sulphate,** $\{(CH_3)_3Pt\}_2SO_4.2H_2O$, by the action of dil. sulphuric acid on the corresponding hydroxide.

As in the case of the hydroxychloroplatinic acids, $H_2Pt(OH)_{6-n}Cl_n$, so with the basic platinic sulphates, there may be a series of **hydroxysulphatoplatinic acids** involving $H_2Pt(OH)_4SO_4$, $H_2Pt(OH)_2(SO_4)_2$ and $H_2Pt(SO_4)_3$. The soln. of platinum in sulphuric acid, free from nitric acid, was found by E. Prost to deposit a brick-red powder $4Pt(OH)_4.Pt(OH)_2SO_4.3H_2O$; and R. Ruer obtained a chocolate-brown powder, $PtO_2.3Pt(OH)_4.Pt(OH)_2SO_4$, containing a small proportion of a platinous salt. There is nothing here to establish the chemical individuality of the products. As indicated above, E. Davy obtained a black mass, by the action of fuming nitric acid on platinic sulphide, which approximated in composition to *platinum dioxysulphate*. PtO_2SO_4, and E. Prost obtained $4Pt(OH)_4.Pt(OH)_2SO_4.3H_2O$ from cold soln., and $Pt_8O_{13}SO_4.16H_2O$ from boiling soln. M. Blondel said that no such compound as PtO_2SO_4 has been proved to exist.

According to M. Blondel, at 0°, hydrated platinic oxide dissolves slowly in sulphuric acid, diluted with its own vol. of water, and there separates from the soln. orange-yellow, microscopic needles of **tetrahydroxysulphatoplatinic acid,** $H_2Pt(OH)_4(SO_4).H_2O$. He said that this represents the composition of what is usually designated normal platinic sulphate. This compound is not soluble in water, and it is decomposed forming free acid and hydrated platinic oxide. It loses 3 mols. of water at 100° to form **hydrodioxysuphatoplatinic acid,** $H_2PtO_2(SO_4)$, which is soluble in water and easily polymerized. Some basic ammines are indicated above.

I. I. Tscherniaeff and A. N. Fedorova prepared **platinic chloroethylenediamino-triamminosulphate,** $[Pten(NH_3)_3Cl]_2(SO_4)_3$, from the corresponding chloride; and A. P. Smirnoff, **platinic trispropylenediaminosulphate,** $[Pt(C_3H_6.N_2H_4)_3](SO_4)_2$. J. Gros, and W. Palmaer prepared **platinic dichlorotetramminosulphate,** $[Pt(NH_3)_4Cl_2]SO_4$, by treating the corresponding nitrate or chloride with warm, dil. sulphuric acid, or with sodium sulphate. Crystals of the *dihydrate* separate out on cooling. The dihydrate loses no water over sulphuric acid, but at 100°, J. Gros, and P. T. Cleve obtained the anhydrous salt. C. Weltzien, and C. Gerhardt also obtained the anhydrous salt, as a crystalline powder, by the action of conc. sulphuric acid on the corresponding nitrate. According to P. T. Cleve, the anhydrous salt is sparingly soluble in hot and cold water; and C. Grimm found the dihydrate to be sparingly soluble in cold water, and freely soluble in hot water; it can be recrystallized by cooling hot soln.; nitric and hydrochloric acids form the corresponding salts. Barium salts precipitate the sulphate; and silver salts produce a turbidity with aq. soln. which have been boiled for a long time. P. T. Cleve prepared **platinic chlorosulphatotetramminosulphate,** $[Pt(NH_3)_4Cl(SO_4)]_2SO_4$, or $[Pt(NH_3)_4Cl_2]SO_4.[Pt(NH_3)_4(SO_4)]SO_4$, by the action of sulphuric acid on the phosphatotetramminochloride. P. T. Cleve prepared **platinic hydroxysulphatote-tramminochloride,** $[Pt(NH_3)_4(OH)(SO_4)]Cl.2H_2O$, by treating the sulphate with one-third molar proportions of barium chloride. The colourless or pale yellow, 4-sided prisms of the *dihydrate* become anhydrous at 100° to 110°. At a higher temp. the salt is decomposed. It is soluble in cold, and very soluble in hot water. Ammonium sulphide gives a dark brown precipitate; conc. soda lye dissolves the salt and no ammonia is evolved when the liquid is boiled; hydrochloric acid forms dichlorotetramminochloride; barium chloride, and sodium phosphate give no precipitates; silver nitrate forms a precipitate at once; ammonium oxalate forms

a white precipitate; potassium chromate, a lemon-yellow precipitate; and potassium dichromate, an orange-red precipitate. Sodium chloroplatinate precipitates orange plates of **platinic hydroxysulphatotetramminochloroplatinate,** $[Pt(NH_3)_4(OH)(SO_4)]_2PtCl_6.2H_2O$. L. A. Tschugaeff and I. I. Tscherniaeff prepared golden yellow **platinous tetramminosulphatohydroxychloroplatinate,** $[Pt(NH_3)_4]_2(SO_4)(PtCl_4)_2(OH)_2$, by the action of ammonium persulphate on Magnus' salt. It is decomposed by washing with water at ordinary temp.; the dry salt oxidizes alcohol to aldehyde; and forms a stable complex with pyridine. K. A. Jensen measured the dipole moment of **platinous ethylsulphinosulphate,** $PtSO_4\{(C_2H_5)S\}_2$.

P. T. Cleve prepared **platinic dibromotetramminosulphate,** $[Pt(NH_3)_4Br_2]SO_4$, by adding bromine to a hot conc. soln. of platinous tetramminosulphate. The lemon-yellow prisms are sparingly soluble in water; silver sulphate precipitates all the bromine, forming $[Pt(NH_3)_4(OH)(SO_4)]_2SO_4.3H_2O$, and with one molar proportion of bromine, there is formed **platinic bromosulphatotetramminosulphate,** $[Pt(NH_3)_4Br(SO_4)]_2SO_4.H_2O$, in sulphur-yellow needles, which are dehydrated at 150°. The salt is freely soluble in hot water; two-thirds of the contained sulphate is precipitated by a soluble barium salt; an excess of sodium bromide forms dibromotetramminobromide; and hydrochloric acid forms bromochlorotetramminochloride. P. T. Cleve prepared **platinic hydroxysulphatotetramminobromide,** $[Pt(NH_3)_4(OH)(SO_4)]Br.2H_2O$, in colourless or pale yellow plates, by mixing equimolar proportions of barium bromide, and the corresponding sulphate; filtering; and evaporating for crystallization. P. T. Cleve also prepared **platinic bromosulphatotriamminobromide,** $[Pt(NH_3)_3(SO_4)Br]Br.H_2O$, by adding bromine to platinous triamminosulphate. The yellow needles dissolve in water, and lose half a mol. of water at 100° to 110°. P. T. Cleve obtained **platinic dibromohexammine-μ-diaminosulphate,** $[Br(NH_3)_3Pt(NH_2)_2Pt(NH_3)_3Br](SO_4)_2.2H_2O$, by the action of sulphuric acid on the corresponding nitrate.

P. T. Cleve reported **platinic diiodotetramminosulphate,** $[Pt(NH_3)_4I_2]SO_4$, by the action of tincture of iodine on platinous tetramminosulphate. The rhombic, dull red prisms are sparingly soluble in water, and the aq. soln. is decomposed when boiled. P. T. Cleve obtained **platinic hydroxyiodotetramminosulphate,** $[Pt(NH_3)_4(OH)I]SO_4.H_2O$, by the action of hydrogen dioxide on a soln. of platinous diiodotetrammino-μ-diimidosulphatotetramminoplatinite. The reddish brown, octahedral crystals are sparingly soluble in water; barium chloride precipitates all the sulphate from the aq. soln. P. T. Cleve prepared **platinic diiodohexammino-μ-diaminosulphate,** $[I(NH_3)_3Pt(NH_2)_2Pt(NH_3)_3I](SO_4)_2$, by the action of dil. sulphuric acid on the corresponding nitrate. O. Carlgren and P. T. Cleve, and P. T. Cleve obtained **platinic diiodohexammine-μ-diimidosulphatotetramminoplatinous sulphate,** $[I(NH_3)_3Pt(NH)_2Pt(NH_3)_3I]SO_4.[Pt(NH_3)_4]SO_4$, by the action of sulphurous acid on the corresponding nitrate. The yellowish crystals are sparingly soluble in boiling water. Barium chloride precipitates from the aq. soln. all the sulphate; it is soluble in 3 per cent. hydrogen dioxide forming the hydroxyiodotetramminosulphate, etc.; dil. hydrochloric acid forms iodochlorotetramminochloride, etc.; and silver nitrate precipitates the iodide. C. W. Blomstrand prepared **platinic sulphatodinitritotetrammine,** $[Pt(NH_3)_4(NO_2)_2SO_4]$.

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§ 29. The Platinum Carbonates

No platinum carbonates have been prepared, but some complex carbonates are known. J. Reiset [1] obtained **platinous tetramminocarbonate** $[Pt(NH_3)_4]CO_3.H_2O$, by the action of atm. carbon dioxide on a soln. of the corresponding hydroxide ; and M. Peyrone, by the action of potassium carbonate on the corresponding chloride at 40° to 50°. By saturating a soln. of the hydroxide with carbon dioxide, J. Reiset obtained **platinous tetramminohydrocarbonate,** $[Pt(NH_3)_4](HCO_4)_2$, as a white, crystalline powder which is not decomposed at 120°. When this salt is boiled with water there is formed **platinous tetramminocarbonatohydrocarbonate,** $[Pt(NH_3)_4]CO_3.[Pt(NH_3)_4](HCO_3)_2$, as a white crystalline powder which begins to decompose at 200°. B. Gerdes obtained **platinic dihydroxyheptamminotetracarbonate,** $Pt_2(NH_3)_7(OH)_2(HCO_3)_4$, by electrolyzing, with an alternating current, for some hours, soln. of ammonium carbonate with platinum electrodes, at 40° to 50°, and cooling. S. G. Hedin described **platinous quaterpyridinetetramminocarbonatohydrocarbonate,** $[Pt(C_5H_5N)_4CO_3.Pt(NH_3)_4](HCO_3)_2.16H_2O$, by treating the sulphate with barium hydroxide, and passing carbon dioxide into the filtered soln. Crystals are obtained by evaporation on the water-bath. The *hexadecahydrate* at 70° passes into the *tetrahydrate,* which decomposes as more water is driven off. S. G. Hedin prepared **platinous carbonatobispyridine,** $[Pt(C_5H_5N)_2CO_3]$; and C. Enebuske, **platinous carbonatobismethylsulphine,** $[Pt\{(CH_3)_2S\}_2CO_3]$.

B. Gerdes obtained **platinic hexamminocarbonate,** $[Pt(NH_3)_6](CO_3)_2$, by electrolyzing with an alternating current an ice-cold soln. of ammonium carbonate, and, after 12 hrs., filtering off the white deposit, washing it with cold water, dis-

solving it in dil. soda lye, diluting the soln. with water and then saturating it with carbon dioxide; and by treating a soln. of the corresponding chloride with sodium carbonate. The white powder, consisting of octahedral crystals, is insoluble in water. L. A. Tschugaeff, and L. A. Tschugaeff and N. Vladimiroff prepared **platinic chloropentamminocarbonate,** $[Pt(NH_3)_5Cl]_2(CO_3)_3$. M. Raewsky prepared **platinic hydroxychlorotetramminocarbonate,** $[Pt(NH_3)_4(OH)Cl]CO_3.H_2O$, by treating the corresponding nitrate with ammonium carbonate, and allowing the mixture to stand for 24 hrs. The caseous precipitate becomes crystalline if the soln. is boiled. P. T. Cleve used sodium carbonate as precipitant. The white or pale yellow, prismatic crystals decompose at 140° to 150°. P. T. Cleve prepared **platinic chlorocarbonatotetramminocarbonate,** $[Pt(NH_3)_4Cl(CO_3)]_2CO_3$, by adding platinic dichlorotetramminonitrate to a boiling soln. of ammonium carbonate. The white powder decomposes when heated without detonation. It dissolves in nitric acid with the evolution of carbon dioxide. P. T. Cleve also prepared **platinic bromocarbonatotetramminocarbonate,** $[Pt(NH_3)_4Br(CO_3)]_2CO_3.2H_2O$, in an analogous way. The crystalline powder loses ammonia at 140°, and at a higher temp. decomposes with a hissing noise. L. A. Tschugaeff and W. Chlopin obtained **platinic hydroxypentamminocarbonate,** $[Pt(NH_3)_5(OH)]_2(CO_3)_3$, by the action of ozone on a mixture of ammonia, ammonium carbonate, and platinous cis-dichlorodiammine.

K. A. Hofmann prepared **platinous thiocarbonatodiammine,** $[Pt(NH_3)_2CS_3]$, by crystallization from a mixture of potassium chloroplatinite, conc. ammonia, and carbon disulphide. In vacuo, over sulphuric acid, the salt becomes anhydrous. The red needles are insoluble in water, aq. ammonia, or soda lye at ordinary temp., but when heated, with the two latter, there is formed a pale reddish-yellow liquid. A soln. of sodium nitroprusside gives no colouration when dil. soda lye is added; and when boiled with methyl iodide, no mercaptan or methylsulphine is formed. Red needles of **platinous dichlorotetramminothiocarbonate,** $[Pt(NH_3)_2Cl_2].[Pt(NH_3)_2CS_2]$, were also prepared. A mixture of ammonium chloroplatinite, aq. ammonia, and carbon disulphide also furnishes black crystals of **platinous amminothiocarbonate,** $[Pt(NH_3)C_2S_5]_2$, which is soluble in soda lye.

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§ 30. The Platinum Nitrates

P. T. Cleve[1] treated platinous tetramminosubhydroxide, $Pt_2(NH_3)_4(OH)_2$, with dil. nitric acid, and obtained a black, amorphous mass of **platinum tetramminosubnitrate,** $2PtNO_3.4NH_3$, or $Pt_2(NH_3)_4(NO_3)_2$. It explodes strongly when heated.

J. J. Berzelius said that some **platinous nitrate,** $Pt(NO_3)_2$, is formed when the greenish brown soln. of hydrated platinous oxide in dil. nitric acid is evaporated to dryness; but some platinic nitrate is formed at the same time, and this the more, the greater the excess of nitric acid employed. J. Reiset crystallized **platinous tetramminonitrate,** $[Pt(NH_3)_4](NO_3)_2$, from the filtrate obtained from mixed soln. of the corresponding chloride and silver nitrate; M. Peyrone obtained it by mixing the corresponding chloroplatinite with nitric acid, and P. T. Cleve, by mixing it with silver nitrate; and B. Gerdes, by electrolyzing with an alternating current a soln.

of ammonium carbonate with platinum electrodes, at 40° to 50°, evaporating the filtrate, precipitating with absolute alcohol, and purifying by dissolution in water and precipitation with alcohol. The salt appears in colourless needles, or monoclinic prisms, which, according to Q. Sella, and A. E. Nordenskjöld, have the axial ratios $a:b:c=1{\cdot}3549:1:1{\cdot}0177$, and $\beta=112°\ 49'$, the (110)- and (101)-cleavages are complete; the (001)-cleavage is incomplete. The salt begins to lose weight at 200°, and it detonates like gunpowder at higher temp. M. Peyrone observed that 100 parts of boiling water dissolve about 10 parts of salt, and J. Reiset added that the aq. soln. is neutral. B. Gerdes observed that water converts the salt into platinic hydroxynitratotetramminonitrate; chlorine, bromine, or iodine forms the corresponding platinic halogeno-nitrate, $[Pt(NH_3)_4X_2](NO_3)_2$; nitric acid containing nitrogen trioxide gives sky-blue octahedral crystals of platinic dinitritotetramminonitrate; and M. Peyrone, that when the salt is boiled with nitric acid and alcohol, a yellowish white, insoluble precipitate is formed, and fumes are given off which excite tears and affect the olfactory organ, and when condensed by cooling with a soln. of the undecomposed salt in nitric acid, a blue substance is obtained.

P. T. Cleve obtained **platinous nitratotriamminonitrate,** $[Pt(NH_3)_3NO_3]NO_3.H_2O$, from a soln. of the corresponding chlorotriamminochloroplatinite and silver nitrate. The white, or pale yellow, crystalline mass decomposes violently when heated; and bromine forms platinic bromodinitratotriamminobromide. A. Werner stated that hydrochloric acid produces platinous chlorotriamminochloride; and potassium chloroplatinite, platinous tetramminochloroplatinite.

J. Reiset prepared **platinous trans-dinitratodiammine,** $[Pt(NH_3)_2(NO_3)_2]$, by the action of silver nitrate on a soln. of the trans-diiododiammine—P. T. Cleve used the dichlorodiammine, in which case, added L. Ramberg, the product is always contaminated with chloride. The pale yellow, crystalline mass decomposes when heated. P. T. Cleve found that the salt dissolves slowly in warm water, and J. Reiset added that the aq. soln. reacts acidic. P. T. Cleve observed that chlorine, and aqua regia convert the salt into platinic tetrachlorodiammine; J. Reiset, that ammonia converts it into platinous tetramminonitrate; and P. T. Cleve, that with the vapour of hyponitrous acid, the soln. becomes blue, and forms dinitritotetrammine. L. Ramberg studied the evolution of ammonia when heated with sodium hydroxide. P. T. Cleve observed that ferric chloride is reduced to ferrous chloride; potassium ferrocyanide gives a green colouration in a few hours, and potassium ferricyanide, a brownish-red colouration; sodium hydrophosphate gives a pale yellow, crystalline precipitate; potassium chromate and dichromate, dark brown precipitates; and sodium chloroplatinate, a dark brown soln., and a precipitate of platinic tetrachlorodiammine. P. T. Cleve also prepared **platinous cis-dinitratodiammine** in an analogous manner. R. Uhlenhuth described **platinous tetrahydroxylaminenitrate,** $[Pt(NH_2OH)_4](NO_3)_2$, prepared in colourless needles, by the action of dil. nitric acid on the hydroxide. F. Hoffmann prepared **platinous dihydroxylaminediamminonitrate,** $[Pt(NH_3)_2(NH_2OH)_2](NO_3)_2$, by the action of barium nitrate on the cis-sulphate.

A. Hantzsch and F. Rosenblatt described **platinous quatermethylaminonitrate,** $[Pt(CH_3NH_2)_4](NO_3)_2$. F. G. Mann, **platinous bis-β-methyldimethylenediaminonitrate,** $[Pt\{CH(CH_3)(CH_2.NH_2)_2\}_2](NO_3)_2$. H. Wolffram, and A. Johnsen, **platinous quaterethylaminenitrate,** $[Pt(C_2H_5NH_2)_4](NO_3)_2$; P. T. Cleve, **platinous bisethylaminediamminonitrate,** $[Pt(C_2H_5NH_2)_2(NH_3)_2](NO_3)_2$, and **platinous trans-bisanilinediamminonitrate,** $[Pt(NH_3)_2(C_6H_5NH_2)_2](NO_3)_2$, and **platinous cis-bisanilinediamminonitrate**; L. A. Tschugaeff and W. Sokoloff; **platinous bispropylenediaminenitrate,** $[Pt\{C_3H_6(NH_2)_2\}_2](NO_3)_2$, from α-propylenediamine; S. G. Hedin, **platinous quaterpyridinenitrate,** $[Pt(C_5H_5N)_4](NO_3)_2$; **platinous quaterpyridinehydronitrate,** $[Pt(C_5H_5N)_4](NO_3)_2.2HNO_3$; **platinous trans-dinitritobispyridine,** $[Pt(C_5H_5N)_2(NO_2)_2]$; also **platinous cis-dinitritobispyridine.** L. Ramberg, **platinous nitratoethylthioglycolatodiammine,** $[Pt(NH_3)_2(NO_3)(CO_2.CH_2.S.C_2H_5)]$; G. T. Morgan and F. H. Burstall obtained a complex with dipyridyl.

C. Enebuske described **platinous quatermethylsulphinenitrate,** $[Pt\{(CH_3)_2S\}_4](NO_3)_2$, and **platinous quaterethylselenine,** $[Pt\{(C_2H_5)_2Se\}_4](NO_3)_2$; **platinous dinitratobismethylsul-**

phine, $[Pt\{(CH_3)_2S\}_2(NO_3)_2]$; J. Petren, C. W. Blomstrand, and H. Löndahl, **platinous trans-dinitratobisethylsulphine,** $[Pt\{(C_2H_5)_2S\}_2(NO_3)_2]$, and **platinous cis-dinitratobisethylsulphine ;** H. Löndahl, **platinous nitratotrisethylsulphinenitrate,** $[Pt\{(C_2H_5)_2S\}_3(NO_3)]NO_3$; C. Rudelius, **platinous trans-dinitratopropylsulphine,** $[Pt\{(C_3H_7)_2S\}_2(NO_3)_2]$, and **platinous cis-dinitratopropylsulphine ;** with normal, and iso-propyl ; and **platinous trans-hydroxynitratopropylsulphine,** $[Pt\{(C_3H_7)_2S\}_2(OH)(NO_3)]$. K. A. Jensen studied the dipole moments of these salts. M. Weibull, and H. Löndahl, **platinous trans-dinitratobutylsulphine,** $[Pt\{(C_4H_9)_2S\}_2(NO_3)_2]$, and **platinous cis-dinitratobutylsulphine,** with normal and iso-butyl. ; N. S. Kurnakoff, **platinous quaterthiocarbamidonitrate,** $[Pt\{CS(NH_2)_2\}_4](NO_3)_2$; J. Petren, **platinous dinitratobisethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2(NO_3)_2]$, **platinous dinitratopyridineethylselenine,** $[Pt(C_5H_5N)\{(C_2H_5)_2Se\}(NO_3)_2]$, and **platinous dinitratoethylsulphinethylselenine,** $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}(NO_3)_2]$; and H. Löndahl, **platinous hydroxynitratobisbenzylsulphine,** $[Pt\{(C_6H_5CH_2)_2S\}_2(OH)(NO_3)]$, and **platinous dinitratoethylenedisulphine,** $[Pt\{(C_2H_4)_2S_2\}(NO_3)_2]$; and L. Ramberg, **platinous nitratoethylthioglycocolatoammine,** $[Pt(NH_3)(CO_2.CH_2.S.C_2H_5)(NO_3)]$.

K. A. Jensen studied trans- **platinous dinitratobistriethylphosphine,** $[Pt\{(C_2H_5)_3P\}_2(NO_3)_2]$. P. Schützenberger and C. Fontaine described **platinous dinitratoethylphosphite,** $[Pt\{P(OC_2H_5)_3\}(NO_3)_2]$, **platinous hydroxynitratosilverphosphite,** $[Pt\{P(OAg)_3\}(NO_3)\{OP(OH)(OAg)\}]$, associated with $[Pt\{P(OAg)_3\}Cl\{OP(OH)(OAg)\}]$; and **platinous dinitratoethylphosphite,** $[Pt\{P(OC_2H_5)_3\}(NO_3)_2]_2$; R. Bunsen, **platinous dinitratoxycacodyl,** $[Pt\{As_2(CH_3)_4O\}NO_3)_2]$; and L. A. Tschugaeff and co-workers ; **platinous dihydrazinoctoethylcarbylaminonitrate,** $[(C_2H_5.NC)_4Pt(N_2H_3)_2Pt(C_2H_5.NC)_4](NO_3)_2.2H_2O$.

J. Petren described **platinous chloronitratobisethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2Cl(NO_3)]$; **platinous chloronitratoethylsulphinethylselenine,** $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}Cl(NO_3)]$; L. Ramberg, **platinous nitratoethylthiolacetatodiammine,** $Pt(NH_3)_2(NO_3)(CO_2.CH_2.S.C_2H_5)$; **platinous nitratoethylthiolacetatomonammine,** $Pt(NH_3)(NO_3)(CO_2.CH_2.S.C_2H_5)$; **sodium dinitratobisethylthiolacetatoplatinite,** $Pt(NO_3)_2(CO_2Na.CH_2.S.C_2H_5)_2$; and **platinous trans-dinitratobisethylthiolacetatodiammine,** $Pt(NH_3)_2(NO_3)_2(CO_2.CH_2.S.C_2H_5)_2.H_2O$; and P. Schützenberger and C. Fontaine, **platinous chloronitratoethylphosphate,** $[Pt\{PO(OC_2H_5)_3\}Cl(NO_3)]_2$.

E. Prost obtained a basic salt **platinosic oxynitrate,** $3PtO_2.Pt(NO_3)_2.5H_2O$, by evaporating a soln. of hydrated platinic oxide in conc. nitric acid. The red mass is insoluble in water. P. T. Cleve's products may be platinosic compounds : **platinosic dihydroxyhexammino-μ-diamidonitrate,** $[(OH)(NH_3)_3Pt(NH_2)_2Pt(NH_3)_3(OH)](NO_3)_4.2H_2O$ obtained by the action of silver nitrate on a boiling soln. of $[I(NH_3)_3Pt(NH_2)_2Pt)NH_3)_3I](NO_3)_4$; or by crystallization from $[(NO_3)(NH_3)_3Pt(NH_2)_2Pt(NH_3)_3(NO_3)](NO_3)_4.4H_2O$. The white, crystalline dihydrate becomes anhydrous at 100° ; and it detonates like gunpowder if heated to a higher temp. It is sparingly soluble in cold water but soluble in hot water. Hydrochloric acid converts it into the dihydroxychloride ; and sulphuric acid, into the dihydroxysulphate, potassium iodide and bromide, and ammonium oxalate give precipitates. If the salt be boiled with nitric acid, there is formed **platinosic nitratohexammino-μ-diamidonitrate,** $[(NO_3)(NH_3)_3Pt(NH_2)_2Pt(NH_3)_3(NO_3)](NO_3)_4.4H_2O$. Water reproduces the original salt. The tetrahydrate becomes anhydrous at 100°. Bromine converts it into **platinosic dibromohexammino-μ-diamidonitrate,** $[Br(NH_3)_3Pt(NH_2)_2Pt(NH_3)_3Br](NO_3)_4.2H_2O$; and with iodine, **platinosic diiodohexammino-μ-diamidonitrate,** $[I(NH_3)_3Pt(NH_2)_2Pt(NH_3)_3I](NO_3)_4.3(\text{or }4)H_2O$. The pale orange crystals become anhydrous at 100°, and detonate at a higher temp. If the dibromsalt is treated with an excess of ammonia, there is formed **platinosic dibromohexammino-μ-diimidonitrate,** $[Br(NH_3)_3Pt(NH)_2Pt(NH_3)_3Br](NO_3)_4$; and if a boiling soln. of platinic diiodotetramminonitrate be treated with an excess of ammonia, **platinosic diiodohexammino-μ-diimidonitrate,** $[I(NH_3)_3Pt(NH)_2Pt(NH_3)_3I](NO_3)_4$, is formed.

J. J. Berzelius obtained a soln. of **platinic nitrate,** $Pt(NO_3)_4$, by dissolving hydrated platinic oxide in nitric acid ; by decomposing a soln. of platinic sulphate with an eq. quantity of barium nitrate and filtering ; and by adding potassium nitrate to a soln. of platinic chloride as long as potassium chloroplatinate is deposited —there is some doubt about the third process. When the dark brown liquid is evaporated, it forms a liquid of the consistency of honey, and it is partially soluble in water leaving as a residue a basic nitrate. L. Wöhler electrolyzed a nitric acid

soln. of platinic nitrate and obtained on the platinum anode an ochre-yellow film, soluble in hydrochloric and sulphurous acids, but insoluble in dil. nitric and sulphuric acids. It has an acidic reaction towards litmus. The deposit is a basic platinic nitrate. E. Koefoed reported **platinic nitrosyltetramminohydronitrate,** $Pt(NH_3)_4(NO)(NO_3)_4.HNO_3$.

B. Gerdes obtained **platinic hexamminonitrate,** $[Pt(NH_3)_6](NO_3)_4$, by the action of nitric acid on the carbonate. The colourless needles are easily soluble in water. I. I. Tscherniaeff and S. I. Chorunshenkoff studied the ionization constants. A. Werner and A. Miolati measured the electrical conductivity of **platinic dinitratotetramminonitrate,** $[Pt(NH_3)_4(NO_3)_2](NO_3)_2$. W. Odling, C. Gerhardt, and P. T. Cleve described **platinic tetranitratodiammine,** $[Pt(NH_3)_2(NO_3)_4]$, prepared by the action of an excess of nitric acid on the dihydroxydinitratodiammine. The colourless or pale yellow powder consists of prisms, insoluble in cold water, sparingly soluble in hot water, and freely soluble in water acidified with nitric acid; the salt crystallizes unchanged from a cooling, hot, aq. soln. Warm hydrochloric acid, and a boiling soln. of potassium chloride form the tetrachloride. P. T. Cleve obtained **platinic trihydroxynitratodiammine,** $[Pt(NH_3)_2(OH)_3(NO_3)]$, by boiling a soln. of the cis-tetrachlorodiammine with silver nitrate; and adding alcohol to the filtrate. The yellowish white, amorphous precipitate is soluble in water. C. Gerhardt, W. Odling, T. Bergman, and P. T. Cleve described **platinic trans-dihydroxydinitratodiammine,** $[Pt(NH_3)_2(OH)_2(NO_3)_2]$, prepared by the action of ammonia on platinic nitrate; and by boiling the tetrachlorodiammine with silver nitrate. The yellowish-white powder, consisting of rhombic or hexagonal plates, is sparingly soluble in cold water, and soluble in hot water. The aq. soln. reddens litmus. Hydrochloric acid precipitates the tetrachloro-salt from a warm soln.; potassium dichromate gives a cinnabar-red precipitate. C. Gerhardt, W. Odling, and O. Carlgren and P. T. Cleve described **platinic dihydroxytetramminonitrate,** $[Pt(NH_3)_4(OH)_2](NO_3)_2$, to be formed by boiling the hydroxynitratotetrammine with ammonia; by the action of hydrogen dioxide on platinous tetramminonitrate; and by the action of barium nitrate on the corresponding sulphate. The white powder consists of rhombic plates. The salt detonates when heated vigorously. The salt is sparingly soluble in cold water but more soluble in hot water—O. Carlgren and P. T. Cleve said that 100 parts of cold water dissolve 0·29 part of salt, and boiling water 2·63 parts. A. Werner obtained no aquo-salt by triturating it with nitric acid. C. Gerhardt said that sulphuric acid turns the dry salt blue, and red nitrous fumes are evolved. The soln. gives white precipitates with ammonium oxalate, sodium hydrophosphate, and sodium carbonate; no precipitate is formed with ammonium chloride; and hydrochloric acid precipitates dichlorotetramminochloride. C. Gerhardt, W. Odling, C. W. Blomstrand, and P. T. Cleve described **platinic hydroxynitratotetramminonitrate,** $[Pt(NH_3)_4(OH)(NO_3)](NO_3)_2$, prepared by warming platinous tetramminosulphate or nitrate with conc. nitric acid; by boiling platinic diiodotetramminonitrate with silver nitrate, or, according to B. Gerdes, by the action of cold water on the dinitritotetramminonitrate. The white crystals decompose with detonation when heated. The salt is sparingly soluble in cold water, easily soluble in hot water, and less soluble in nitric acid. Hydrochloric acid slowly forms dichlorotetramminonitrate; ammonium chloride gives no precipitate; conc. sulphuric acid forms sulphatotetramminosulphate; nitric acid gives a white precipitate; neither potash lye nor aq. ammonia gives a precipitate in sat. soln.; aq. ammonia forms dihydroxytetramminonitrate; ammonium carbonate forms carbonatonitratotetramminocarbonate; ammonium oxalate gives a white precipitate; sodium phosphate forms phosphatotetramminonitrate; potassium dichromate forms dinitratotetramminedichromate; potassium chromate gives a yellow precipitate. P. T. Cleve prepared **platinic dihydroxynitratotriamminonitrate,** $[Pt(NH_3)_3(OH)_2(NO_3)]NO_3.H_2O$, from silver nitrate and platinic bromodinitratotriamminobromide. The white crystalline powder is soluble in water. F. M. Jäger studied the crystals of **platinic trisethylenediaminonitrate,**

$Pten_3(NO_3)_4.2H_2O$. L. A. Tschugaeff and co-workers prepared **platinic carbylaminohydrazinonitrate.**

A. P. Smirnoff prepared **platinic trispropylenediaminonitrate,** $[Pt(C_3H_6.N_2H_4)_3](NO_3)_4$. P. T. Cleve described **platinic hydroxyacetatotetramminonitrate,** $[Pt(NH_3)_4(OH)(C_2H_3O_2)](NO_3)_2$; L. Ramberg, **platinic bisethylthioglycolatodiamminonitrate,** $[Pt(NH_3)_2(H.CO_2.CH_2.S.C_2H_5)_2](NO_3)_2.H_2O$; C. Rudelius, **platinic dihydroxydinitratobispropylsulphine,** $[Pt\{(C_3H_7)_2S\}_2(OH)_2(NO_3)_2]$; J. Petren, **platinic tetranitratobisethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2(NO_3)_4]$, and **platinic dihydroxydinitratobisethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2(OH)_2(NO_3)_2]$.

W. J. Pope and S. J. Peachey prepared **trimethyl platinic nitrate,** $(CH_3)_3Pt(NO_3)$, by the action of warm conc. nitric acid on the corresponding hydroxide.

L. A. Tschugaeff and W. Chlopin prepared **platinic hydroxypentamminonitrate,** $[Pt(NH_3)_5(OH)](NO_3)_3$; and L. A. Tschugaeff, W. Palmaer, and L. A. Tschugaeff and N. Vladimiroff, **platinic chloropentamminonitrate,** $[Pt(NH_3)_5Cl](NO_3)_3$, in colourless prisms; and **platinic hydroxypentamminonitrate,** $[Pt(NH_3)_5(OH)](NO_3)_3$, in colourless, glistening scales. I. I. Tscherniaeff and A. N. Fedorova, **platinic chloroethylenediaminotriamminonitrate,** $[Pten(NH_3)_3Cl](NO_3)_3$, by the action of nitric acid on the chloride. W. Odling, and P. T. Cleve described **platinic dinitratotetramminochloride,** $[Pt(NH_3)_4(NO_3)_2]Cl_2$, prepared by the action of hydrochloric acid on a hot soln. of the hydroxynitratotetramminonitrate. It is deposited as a *monohydrate*, but becomes anhydrous at 100°. It is soluble in cold water, and very soluble in hot water. Ammonium chloride gives no precipitate in aq. soln.; potassium chromate precipitates the dinitrato-chromate; silver nitrate precipitates all the chlorine as silver chloride; and hydrochloroplatinic acid forms **platinic dinitratotetramminochloroplatinate,** $[Pt(NH_3)_4(NO_3)_2]PtCl_6.2H_2O$. J. Gros, M. Raewsky, W. Odling, M. Peyrone, E. A. Hadow, A. Grünberg, and P. T. Cleve prepared **platinic dichlorotetramminonitrate,** $[Pt(NH_3)_4Cl_2](NO_3)_2$, by warming platinous tetramminochloroplatinite or the corresponding chloride with nitric acid; P. T. Cleve, by passing chlorine into a conc. soln. of platinous tetramminonitrate; and C. Gerhardt, from the mother-liquor obtained in the preparation of hydroxychlorotetramminonitrate. The salt is sometimes called *Gros' nitrate;* and its constitution was discussed by J. J. Berzelius, C. Gerhardt, C. Claus, C. Weltzien, H. Kolbe, C. Grimm, C. H. D. Bödeker, H. Schiff, C. W. Blomstrand, W. Odling, A. Geuther, and C. F. Rammelsberg. The colourless or pale yellow prismatic crystals were found by C. F. Rammelsberg to be monoclinic, and to have the axial ratios $a : b : c = 0{\cdot}7544 : 1 : 0{\cdot}7190$, and $\beta = 109° 0'$. M. Raewsky said that the salt decrepitates when heated, and then gives off ammonium chloride, water, etc., leaving platinum behind. N. S. Kurnakoff found the index of refraction of a soln. of concentration 2·712, or sp. gr. 1·01753 at 14·1°/4° to be 1·33417, 1·33651, and 1·33848, respectively, for Li-, Na-, and Tl-light; the mol. refraction with the μ-formula is therefore 105·4 for Na-light. A. Werner and A. Miolati found the conductivity of soln. with a mol of salt in 250, 500, 1000, and 2000 litres to be, respectively, 204·2, 222·0, 233·8, and 243·7.

According to W. Odling, the salt is freely soluble in water. P. T. Cleve found that potassium iodide forms platinic diiodotetramminoiodide; J. Gros, that hydrogen sulphide precipitates very little platinum; P. T. Cleve, that sulphur dioxide forms platinous tetramminohydrosulphite; E. A. Hadow, that sodium sulphate forms the dichlorotetramminosulphate; P. T. Cleve, that an excess of aq. ammonia forms a pale yellow soln., which on evaporation furnishes a glassy mass which when heated detonates like gunpowder; J. Gros, M. Raewsky, and P. T. Cleve, that potash lye, particularly when boiling develops ammonia, leaving a soln. which, on standing, furnishes a white powder which detonates when heated; J. Gros, that calcium hydroxide acts on the solid giving very little ammonia; J. Gros, and P. T. Cleve, that alkali carbonates give a precipitate of hydroxychlorotetramminocarbonate, and ammonium carbonate, chlorocarbonatotetramminocarbonate; P. T. Cleve, that sodium phosphate precipitates phosphatotetramminochloride; P. T. Cleve, and M. Raewsky, that silver nitrate in the cold makes the soln. turbid,

and when the mixture is boiled for half an hour, about half the chloride is precipitated as silver chloride, and hydroxychlorotetramminonitrate is formed, more chloride is precipitated if the soln. be boiled for some days; and P. T. Cleve, that potassium chromate and dichromate precipitate yellow chlorochromates, and hydrochloroplatinic acid forms dichlorotetramminochloroplatinate. L. A. Tschugaeff prepared **platinic aminochlorotetramminonitrate,** $[Pt(NH_3)_4(NH_2)Cl](NO_3)_2$.

M. Raewsky prepared **platinic hydroxychlorotetramminonitrate,** $[Pt(NH_3)_4(OH)Cl](NO_3)_2$, by boiling platinous tetramminochloroplatinite with an excess of nitric acid until red fumes are no longer evolved, the precipitate which forms when the liquid is cooled is dissolved in boiling water, and the soln. is evaporated over sulphuric acid in vacuo. The re-crystallization is repeated 4 times and finally the product is dried at 120°. C. Gerhardt obtained it by boiling silver nitrate with platinic dichlorotetramminochloride, E. A. Hadow used the dichlorotetramminonitrate. C. W. Blomstrand, W. O. Odling, M. Raewsky, C. Gerhardt, and E. A. Hadow discussed the constitution of what is called *Raewsky's nitrate.* The white powder consists of six-sided plates. When heated, water, etc., are evolved with a feeble detonation. The salt is soluble in cold water, and more easily so in hot water. Hydrochloric acid precipitates the dichlorotetramminochloride; ammonium chloride forms the chloride; sulphuric acid or alkali sulphates give no precipitate except that sodium sulphate gives a precipitate after some time; nitric acid, the chloronitratotetramminonitrate; sodium phosphate gives a crystalline precipitate; potassium hydroxide forms a yellow liquid and develops ammonia; alkali carbonates, and ammonium carbonate give a white precipitate of the carbonate; acetic, tartaric, and succinic acids give no precipitate; silver nitrate gives no precipitate with cold soln. nor with cold soln. that have been boiled for half an hour but with 10 hrs. boiling, about two-thirds of the chlorine is precipitated as silver chloride; potassium chloroplatinite gives a green crystalline precipitate; and platinous chloride, in dil. nitric acid soln., gives a copper-coloured precipitate.

P. T. Cleve described **platinic chloronitratotetramminonitrate,** $[Pt(NH_3)_4(NO_3)Cl](NO_3)_2$, to be formed by the action of an excess of conc. nitric acid on the hydroxychlorotetramminonitrate. The crystalline powder consists of rhombic prisms which are hydrolyzed by water to hydroxychlorotetramminonitrate. P. T. Cleve obtained **platinic chlorodinitratotriamminochloride,** $[Pt(NH_3)_3(NO_3)_2Cl]Cl$, by the action of nitric acid on platinous chlorotriamminochloroplatinite. The white crystals are insoluble in water. M. Peyrone reported **platinic trichloronitratodiammine,** $[Pt(NH_3)_2(NO_3)Cl_3]$, to be formed by the action of nitric acid on platinous cis-dichlorodiammine. The yellow prisms decompose at 200°; 100 grms. of a sat. aq. soln. contain 1·8 grms. of salt, and a boiling soln., 6·0 grms.; boiling hydrochloric, nitric, or oxalic acid does not dissolve the salt; but hot sulphuric acid develops chlorine; aq. ammonia dissolves the salt; ammonium oxalate, and sodium sulphate give no precipitate; the salt is insoluble in alcohol, and in ether; hot potash lye develops ammonia; and silver nitrate precipitates part of the chlorine. E. A. Hadow prepared **platinic dichlorodinitratodiammine,** $[Pt(NH_3)_2(NO_3)_2Cl_2]$, in association with platinous tetramminochloroplatinite (*q.v.*). P. T. Cleve prepared **platinic chlorodinitritonitratodiammine,** $[Pt(NH_3)_2(NO_2)_2(NO_3)Cl]$, by the action of hydrochloric acid on a conc. soln. of the dinitritodinitratodiammine. A. Wurtz reported **platinic dichloroquatermethylaminenitrate,** $[Pt(CH_3NH_2)_4Cl_2](NO_3)_2$; S. G. Hedin described **platinic dichloroquaterpyridinenitrate,** $[Pt(C_5H_5N)_4Cl_2](NO_3)_2$, and **platinic dichloroquaterpyridinehydronitrate,** $[Pt(C_5H_5N)_4Cl_2](NO_3)_2.2HNO_3.2H_2O$; and H. Löndahl, **platinous chloronitratobisbutylsulphine,** $[Pt\{(C_4H_9)_2S\}_2(NO_3)Cl]$.

P. T. Cleve obtained **platinic dibromotetramminonitrate,** $[Pt(NH_3)_4Br_2](NO_3)_2$, by dropping bromine into a conc. soln. of platinous tetramminonitrate, and then boiling the liquid; pale yellow, 4-sided plates or prisms separate from the cooling soln. The salt decomposes between 180° and 185°. It is sparingly soluble in cold

water, but freely soluble in hot water; it dissolves in aq. ammonia; ammonium bromide precipitates the red bromide; ammonium chloride precipitates the chloride; silver nitrate precipitates silver bromide in cold soln., and with boiling soln., the hydroxybromotetramminonitrate is formed; potash lye forms an orange-red soln. but no ammonia is given off, but that gas is evolved with the heated lye; alkali carbonates give a mixed precipitate; sodium phosphate precipitates phosphatotetramminobromide; and potassium ferrocyanide gives a red precipitate.

P. T. Cleve prepared **platinic bromonitratotetramminonitrate,** $[Pt(NH_3)_4(NO_3)Br](NO_3)_2$, by the action of an excess of conc. nitric acid on the hydroxybromotetramminonitrate. The lemon-yellow powder contains rhombic prisms. The salt is hydrolyzed by water to hydroxybromotetramminonitrate. A. R. Klien studied the action of water, acids, and alkaline soln. P. T. Cleve reported **platinic hydroxydinitratotriamminobromide,** $[Pt(NH_3)_3(NO_3)_2(OH)]Br.H_2O$, by the action of the theoretical amount of silver nitrate on the bromodinitratoamminobromide. The straw-yellow scales are soluble in water, and an aq. soln. of silver nitrate precipitates part of the bromide from cold soln., and all is removed from boiling soln. P. T. Cleve also obtained **platinic bromodinitratotriamminobromide,** $[Pt(NH_3)_3(NO_3)_2Br]Br.H_2O$, by the action of bromine on platinous nitratotriamminonitrate. The golden yellow scales are soluble in water, and silver nitrate precipitates all the bromine from boiling soln., and forms the dihydroxynitratotriamminonitrate. L. A. Tschugaeff prepared **platinic chloroamidotetramminonitrate,** $[Pt(NH_3)_4(NH_2)Cl](NO_3)_2$; and B. E. Dixon, **platinic dichloroamidotriamminonitrate,** $[Pt(NH_3)_3(NH_2)Cl_2]NO_3$. S. G. Hedin described **platinic dibromoquaterpyridinenitrate,** $[Pt(C_5H_5N)_4Br_2](NO_3)_2$, **platinic dibromoquaterpyridinehydronitrate,** $[Pt(C_5H_5N)_4Br_2](NO_3)_2.HNO_3.3H_2O$, **platinic bromonitratoquaterpyridinehydronitrate,** $[Pt(C_5H_5N)_4(NO_3)Br](NO_3)_2.HNO_3$; and **platinic dibromodinitratobisethylselenine,** $[Pt\{(C_2H_5)_2Se\}_2(NO_3)_2Br_2]$.

P. T. Cleve prepared **platinic diiodotetramminonitrate,** $[Pt(NH_3)_4I_2](NO_3)_2$, by the action of an excess of tincture of iodine on a soln. of platinous tetramminonitrate. The dark brown precipitate crystallizes from its hot, aq. soln. in dark brown scales. When the aq. soln. is boiled, iodine is given off, and when the soln. is shaken with mercury, mercuric iodide is formed. Ammonia converts the boiling aq. soln. into **platinum diiodohexammino-μ-diimidonitrate,** $[I(NH_3)_3Pt(NH)_2Pt(NH_3)_3I](NO_3)_2$—*vide supra,* platinosic salts. P. T. Cleve, and O. Carlgren and P. T. Cleve obtained **platinic dibromonitratotriamminoiodide,** $[Pt(NH_3)_3Br_2(NO_3)]I$, in yellowish-white needles, by gradually adding bromine to a hot soln. of platinum diiodohexammine-μ-diamidonitrate. K. Johansson, and O. Carlgren and P. T. Cleve prepared **platinum dinitratohexammino-μ-diimidosulphate,** $[(NO_3)(NH_3)_3Pt(NH)_2Pt(NH_3)_3(NO_3)]SO_4$, by the action of the theoretical proportion of silver nitrate on the corresponding diiodo-sulphate—*vide supra,* the platinosic salts.

P. T. Cleve obtained **platinic bromonitratotetramminosulphate,** $[Pt(NH_3)_4(NO_3)Br]SO_4.H_2O$, in small rhombic prisms and plates, by the action of conc. sulphuric acid on hydroxybromotetramminonitrate; and also **platinic hydroxysulphatotetramminonitrate,** $[Pt(NH_3)_4(OH)(SO_4)]NO_3$, by treating the sulphate with the theoretical proportion of barium nitrate. P. T. Cleve obtained **platinous chloronitratotetramminosulphate,** $[Pt(NH_3)_4(NO_3)Cl]SO_4$, by the action of conc. sulphuric acid on the hydroxychlorotetramminonitrate. The white prismatic crystals are sparingly soluble in cold water, and freely soluble in hot water; and an excess of ammonium bromide forms dibromotetramminobromide. P. T. Cleve prepared **platinic carbonatonitratotetramminocarbonate,** $[Pt(NH_3)_4(NO_3)(CO_3)]_2CO_3$, in white prisms or scales, by boiling an aq. soln. of the hydroxynitratotetramminonitrate with ammonium carbonate; and **platinic bromocarbonatotetramminocarbonate dibromotetramminonitrate,** $[Pt(NH_3)_4(CO_3)Br]_2CO_3.2[Pt(NH_3)_4Br_2](NO_3)_2$, in egg-yellow needles, by mixing boiling soln. of the dibromotetramminonitrate with sodium carbonate until the precipitate first formed redissolves, and cooling the liquid filtered hot.

P. T. Cleve, E. A. Hadow, B. Gerdes, and E. Koefoed prepared **platinic dinitritotetramminonitrate,** $[Pt(NH_3)_4(NO_2)_2](NO_3)_2$, by passing nitrous fumes into a soln. of platinous tetramminosulphate; by the action of sodium nitrite on a soln. of platinous tetramminonitrate; P. T. Cleve, **platinic iodonitritotetramminonitrate,** $[Pt(NH_3)_4(NO_2)I](NO_3)$, by the action of dil. nitric acid (1 : 1) on platinum diiodohexammino-μ-diimidoiodide; P. T. Cleve, **platinic dinitritodinitratodiammine,** $[Pt(NH_3)_2(NO_2)_2(NO_3)_2]$, by boiling platinous dinitritodiammine with nitric acid; and P. T. Cleve, **platinic chlorodinitritonitratodiammine,** $[Pt(NH_3)_2(NO_2)_2(NO_3)Cl]$, by the action of hydrochloric acid on conc. soln. of the dinitritodinitratodiammine.

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§ 31. Platinum Phosphates

B. E. Dixon[1] prepared **platinous hexamminohydroxyhydrophosphate**, $[Pt(NH_3)_6]_2(OH)_2(HPO_4)_2.2H_2O$, by the action of ammonium hydrophosphate, on an ammoniacal soln. of the hexamminochloride. According to P. T. Cleve, phosphoric acid does not give a precipitate with soln. of platinous tetrammino-chloride, but if the soln. be first neutralized with ammonia sometimes a precipitate of **platinous ammonium tetramminohydrophosphate** $[Pt(NH_3)_4]NH_4(PO_4).(NH_4)_3PO_4.4(NH_4)H_2PO_4.H_2O$, is formed. The powder consists of acicular crystals which melt at 100° with the loss of ammonia ; and ammonia is lost when the salt is confined over sulphuric acid. If a soln. of the salt in hot water be evaporated on the water-bath until ammonia is no longer evolved, rectangular plates of $[Pt(NH_3)_4]HPO_4.2(NH_4)H_2PO_4.2H_3PO_4.9H_2O$, are formed. If the addition of phosphoric acid to a neutralized soln. of platinous tetramminochloride gives no precipitate, the addition of alcohol furnishes a precipitate which, when recrystallized from hot water, consists of colourless or pale yellow plates of **platinous tetramminohydrophosphate**, $4[Pt(NH_3)_4]HPO_4.5H_2O$. The crystals are stable in air, and lose 4 mols. of water at 115°. The salt is sparingly soluble in cold water, but freely soluble in hot water ; bromine precipitates platinic phosphatotetramminobromide from the hot soln. ; and silver nitrate gives a yellow precipitate. H. Alexander precipitated **platinous tetrahydroxylaminephosphate**, $[Pt(NH_2OH)_4]_3(PO_4)_2.3H_2O$, by adding sodium hydrophosphate to a soln. of the corresponding chloride. F. Hoffmann reported **platinous cis-dihydroxylaminodiamminohydrophosphate**, to be formed, in pale yellow needles, when a soln. of the cis-chloride is treated with a soln. of sodium phosphate. C. Enebuskc obtained **platinous phosphatobismethylsulphine**, $[Pt\{(CH_3)_2S\}_2(PO_4)_2].nH_2O$, as a precipitate, by adding a conc. soln. of sodium phosphate to one of the corresponding sulphate. C. W. Blomstrand also prepared **platinous phosphatobisethylsulphine**, $[Pt\{(C_2H_5)_2S\}_2(PO_4)_2].4H_2O$.

P. T. Cleve prepared **platinosic dihydroxyhexammino-μ-diamidohydrophosphate**, $[(OH)(NH_3)_3Pt(NH_2)_2Pt(NH_3)_3(OH)](HPO_4)_2$, from a soln. of the corresponding nitrate and sodium hydrophosphate, and **platinosic diiodohexammino-μ-diamidohydrophosphate**, $[I(NH_3)_3Pt(NH_2)_2Pt(NH_3)_3I](HPO_4)_2$, from a soln. of the corresponding nitrate and sodium hydrophosphate.

A. V. Kroll observed that in the preparation of calcium ultraphosphates when the vapour of phosphorus pentoxide acts on platinum, a brown powder or iridescent film is produced which readily dissolves in water forming a deep blue liquid. When it is heated, phosphorus pentoxide is evolved. By analogy with silver ultraphosphate, or triphosphate, $Ag_2O.3P_2O_5$—**8.** 22, 24, it was assumed that **platinous ultraphosphate** or **platinous triphosphate**, $PtO.3P_2O_5$, is formed.

According to W. H. Wahl, hydrated platinic oxide dissolves in warm phosphoric acid to form a wine-yellow, or cherry-red soln. of **platinic phosphate.** The solubility of the hydrated dioxide in the cold acid is small. The solubility is greater, the more conc. the soln. of acid. The salt has not been isolated. By adding ammonia to the soln. of hydrated platinic oxide in phosphoric acid until the reaction is alkaline, W. H. Wahl obtained a soln. of **ammonium phosphatoplatinate**, but he did not isolate the salt.

M. Raewsky prepared **platinic phosphatotetramminochloride**, $[Pt(NH_3)_4(PO_4)]Cl.2H_2O$, by treating the hydroxychlorotetramminonitrate with sodium phosphate ; and P. T. Cleve, by treating the dichlorotetramminonitrate with an excess of sodium hydrophosphate, and drying the washed product at 100° or over sulphuric acid. The pale yellow, crystalline powder, consisting of rhombohedral or rhombic plates, loses half a mol. of water at 120° to 150°. It is insoluble in cold water, and sparingly soluble in hot water. P. T. Cleve obtained **platinic phosphatotetrammino-bromide**, $[Pt(NH_3)_4(PO_4)]Br.2H_2O$, by treating the dibromotetramminonitrate in a similar manner. The dirty yellow powder consists of 6-sided prisms or plates. P. T. Cleve reported **platinic dibromotetramminodihydrophosphate**, $[Pt(NH_3)_4Br_2]$-

$H_2PO_4.2H_2O$, to be formed by the action of bromine on platinous tetrammino-hydrophosphate. The lemon-yellow needles or prisms become anhydrous at 100°. The salt is soluble in hot water. B. E. Dixon prepared **platinic chloroamidotetramminohydroxydihydrophosphate,** $[Pt(NH_3)_4Cl(NH_2)](OH)H_2PO_4)$; **platinic chloroamidotetramminobisdihydrophosphate,** $[Pt(NH_3)_4Cl(NH_2)](H_2PO_4)_2$; **platinic dichlorotetramminohydroxydihydrophosphate,** $[Pt(NH_3)_4Cl_2](OH)(H_2PO_4).2H_2O$; **platinic chlorohydrophosphatotetramminohydroxide,** $[Pt(NH_3)_4(HPO_4)Cl]OH$; and **platinic chlorohydrophosphatoamidotriammine,** $[Pt(NH_3)_3(NH_2)Cl(HPO_4)]$. P. T. Cleve also prepared **platinic phosphatotetramminonitrate,** $[Pt(NH_3)_4(PO_4)]NO_3.H_2O$, by the action of an excess of sodium hydrophosphate on hydroxynitratotetramminonitrate. The white needles decompose at 140° to 150°. The salt is sparingly soluble in water. For some phosphatoalkylsulphines, *vide supra*, the complex halides, etc.

R. E. Barnett prepared **platinic pyrophosphate,** PtP_2O_7, by passing the vapour of phosphorus pentoxide over spongy platinum, removing the metaphosphoric acid by water, and then washing with aqua regia until nothing further is dissolved, washing, and drying. The product is a pale greenish-yellow powder, apparently amorphous ; its density is 4·856. It is stable at a red heat, darkening somewhat but regaining its original colour on cooling. In contact with a flame, however, it is readily reduced, giving off white fumes. It is insoluble in water and unaffected by aqueous acids and alkalies, although easily decomposed by fusion with sodium-potassium carbonate. It is insoluble in a solution of sodium pyrophosphate. Chlorine and bromine appear to be without action on it. It is gradually decomposed by solutions of hydrogen sulphide or alkali sulphides. P. T. Cleve obtained **platinic hydroxynitratotetramminopyrophosphate,** $[Pt(NH_3)_4(OH)(NO_3)]P_2O_7.H_2O$, by adding a soln. of sodium pyrophosphate to one of the phosphatotetramminonitrate.

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GENERAL INDEX

(Compiled by Miss E. M. Rigby)

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